

Enrico Drioli
Lidietta Giorno
Editors

Encyclopedia of Membranes



SpringerReference

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Encyclopedia of Membranes

With 968 Figures and 185 Tables

 **Springer** Reference

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Preface

The *Encyclopedia of Membranes* is a reference work that covers all aspects of membrane science and technology, from basic phenomena to the most advanced applications and future perspectives. It is aimed at students, graduate students, academic and industrial researchers, and practitioners.

The *Encyclopedia of Membranes* is organized around a list of searchable *Entries* or *Terms*, in alphabetical order, giving the user fast and easy access to terminology, description, theory, and application of membrane science.

Entries range from one to several printed pages and are written by one or multiple authors.

Authors are both from academic institutions, research agencies, and industries.

The development of the Encyclopedia is undertaken by the Chief Editors, Prof. Enrico Drioli and Dr. Lidiatta Giorno, responsible for the selection of the topics, the terms, and the quality of the contributions. An Advisory Board was identified to discuss major items and promote holistic vision of the work. An Editorial Board assisted the Chief Editors in their activities.

The *Encyclopedia of Membranes* is a landmark work covering the science, technology, and application of membranes, membrane operations, and related fields.

A membrane is a nanostructured/functionalized thin barrier that controls the exchange phenomena (matter and energy) between two different phases, both through the external forces and under the effect of fluid properties, and also through the intrinsic characteristics of the membrane material itself.

Membranes are used in various applications. They differ widely in their structure, in their function, and the way they are operated. Membranes may be biological or synthetic, solid or liquid, homogeneous or heterogeneous, isotropic or anisotropic, and it can be a fraction of a micrometer or various millimeters thick. The application of different membrane structures and driving forces caused a number of rather different membrane processes such as micro-, ultra-, and nanofiltration, reverse osmosis, dialysis and electrodialysis, pervaporation, gas separation, membrane contactors (membrane distillation, membrane crystallizer, membrane strippers, membrane scrubbers, membrane condenser, membrane emulsifier), membrane reactors, catalytic membrane reactor, etc.

In various fields, membrane operations are already dominant technologies. Interesting examples are in the seawater desalination, in wastewater treatment

and reuse, and in biomedical applications. They are of interest in all sectors strategic for a sustainable development. They are clean, safe, require low energy input, and suitable to promote process intensification. Practically all typical unit operations of process engineering might be redesigned as *membrane unit operations*.

Membrane operations are largely present, for example, in the following fields:

- *Water treatment and purification*
- *Energy*
- *Gas separation*
- *Solvent treatment and purification*
- *Petrochemical industry* (where the integration of different membrane operations has promising applications)
- *Environment*
- *Agro-food and packaging*
- *Biotechnology*
- *Tissue engineering and regenerative medicine*
- *Biorefinery*
- *Pharmaceutical and cosmetic*
- *Microelectronics (OLEDS)* (which is becoming an area of interesting applications)

Other fields that will exploit more and more membranes' unique features include:

- *Sensors*
- *Micromanufacturing*
- *Responsive materials*
- *Safety and security*
- *Space*

The large spectrum of challenges membrane operations contribute to face today and their strong multidisciplinary character suggested to develop this work on membrane science and membrane engineering.

Enrico Drioli
Lidietta Giorno

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We also wish to express grateful thanks to the members of the advisory board for their kind availability as well as to all authors for their invaluable contribution to the work.

Enrico Drioli
Lidietta Giorno

Editors Biography



Enrico Drioli Emeritus Professor, University of Calabria, Rende, Italy

Career

Distinguished Visiting Professor, Faculty of Engineering and Information Technology, University of Technology Sydney, Australia (January 2016)

Distinguished Adjunct Professor, Center of Excellence in Desalination Technology, King Abdulaziz University, Jeddah, Saudi Arabia (2012)

WCU (World Class University) Distinguished Visiting Professor, Department of Energy Engineering, Hanyang University, Seoul Korea (2009)

Emeritus Professor, School of Engineering of the University of Calabria (2012)

Professor of Chemistry and Electrochemistry at the School of Engineering of the University of Naples (since 1968–1982)

Professor at the School of Engineering of the University of Calabria (1981–2011)

Dean of the School of Engineering of the University of Calabria (1982–1985)

Founding Director of the Institute on Membrane Technology (ITM) of CNR (from 2011)

Director of the Institute on Membranes and Chemical Reactors of the National Research Council (1993–2001)

Director of the Institute on Membrane Technology (ITM) of CNR (2002–2008)

Research Interest

Membranes in artificial organs, integrated membrane processes, membrane preparation transport phenomena, membrane distillation and membrane contactors, catalytic membrane, and catalytic membrane reactors.

Biography

Coordinator of the European Erasmus Mundus Doctorate in Membrane Engineering (EUDIME).

Scientific Coordinator of various international contracts/agreements: ITM-CNR-KACST, Hydrophobic membrane preparation for membrane contactors application; ITM-CNR-KISR (Kuwait Institute for Scientific Research), Evaluation of the potentialities of the membrane distillation technology for desalting de-oiled filtered high concentrated saline waters; RHODIA; etc.

Member of the Scientific Advisory Panel (SAP) for the KAUST Water Desalination and Reuse (WDR) Center from 2010

MIAC International Award for International Collaboration and Promotion (October 2015)

Award with the Academician Semenov Medal of Russian Academy of Engineering Science (2014)

Honorary Membership of the Czech Society of Chemical Engineering (2012)
2011, “Richard Maling Barrer Prize” of the EMS, for his “outstanding contributions to membrane science and technology”

2009, Doctorate Honoris Causa from University of Paul Sabatier of Toulouse, France

2005, International Cooperation Honor Award, Membrane Industry Association of China (MIAC) for special dedication to International Cooperation between China and Europe in the field of membrane science and technology

2005–Present, Guest Professor, Jiangsu Polytechnic University, China

1999, Honorary President, European Membrane Society

1992, Doctorate Honoris Causa in Chemistry and Chemical Technology, Russian Academy of Science

1991, Honorary Professor, China Northwest University in Xi'an, Shaanxi, China

1982–1998, President, European Society of Membrane Science and Technology (European Membrane Society)

Advisory Board of *Journal of Membrane Science*, *Polish Journal of Chemical Technology*; Editorial Board of various other international scientific journals.

Executive Editor: *Applied Water Science* Journal, Springer Berlin Heidelberg (Germany) and *Membrane Water Technology*, Techno Press (Korea).

Editor of more of 750 scientific papers, 22 patents, and 24 books



Lidietta Giorno is serving as the Director of the Institute on Membrane Technology of the National Research Council of Italy, ITM-CNR, since 2009.

Her research expertise include membrane bioengineering, biocatalytic membrane reactors, integrated membrane systems for bioseparations and bioconversions, downstream processing based on molecular separation, membrane chirotechnology, membrane emulsifier, and integrated membrane operations for water treatment. She has been involved in membrane science and engineering research and development for some 25 years, and in research cooperations at European and international levels.

She was awarded the international “Guido Dorso Award” for research in 2011, sponsored by the Italian Senate and the University of Naples Federico II. She was awarded the Sapio Red Carpet Award in 2016 among female scientists of highest scientific profile who are engaged for the development of the country.

She worked abroad in the USA at Sepracor Inc. in 1992, in the Netherlands at ATO-DLO in 1994, and in France at The University of Compiègne in 1997–2000. She is Visiting Professor at Tianjin University of Science and Technology, China, since 2008.

Lidietta Giorno is coeditor of 8 books, over 110 peer-reviewed scientific papers in international journals, and coeditor of the *Encyclopedia of Membranes*, Springer, 2016. She is member of the editorial board of scientific journals, member of the referee pool of scientific journals and research agencies, and member of international committees and several scientific societies.

She has served as member of the Board of Directors of the European Membrane House (EMH, Belgium), formed to continue the activity of the NanoMemPro Network of Excellence funded by the European Commission within the FP6.

She has served on the European Membrane Society Council as the President of the EMS Council and the Editor of the EMS Membrane Newsletter. She was nominated Honorary Member of the European Membrane Society in 2014.

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Ab Initio Calculation

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Although the term *ab initio* usually indicates calculations based on first principles, either they are related to classical or to quantum mechanics, this term is generally used when it refers to calculations based on quantum mechanics first principles (Szabo and Ostlund 1994). Thus, if the d'Alembert equation is used to describe a force balance, in which the expression of the forces is only expression of chemical-physical average properties (values obtained as average of microscopic properties) without any use of empirical adjustable parameters, the calculation can also be defined *ab initio*. As mentioned, in general, the term *ab initio* is used when the calculations are performed by using the Schrödinger equation or rather an eigenvalue equation for the quantum system. However, attention must be paid to the quantities or potential operators that define the eigenvalue equations. In fact, if the operators in the Hamiltonians are defined using experimental data or by means of fitting procedure, then the calculation should not be defined *ab initio* but semiempirical (Clementi and Corongiu 1995). The density functional theory (Parr and Yang 1989) is a controversial case, since in principle,

it is an *ab initio* theory, but various potentials defining the quantum system are obtained by using empirical data. For example, hybrid potentials are linear combinations of pure potentials. The coefficients of the linear combinations are obtained using experimental data. Nevertheless, other potentials are obtained from the thermodynamic theory of electron gas (statistical thermodynamics); thus the latter can be considered *ab initio*. For this reason also the density functional theory is considered an *ab initio* methodology. Summarizing, two broad theoretical methods can be identified: those that make use of adjustable parameters that should be to be defined each time, *ad hoc*, depending on the system studied and those that do not use *ad hoc* parameters which only refer to the first principles and are known as the *ab initio* methods.

Particular attention should be given on multiscale simulations in which parameters provided by sub and nanoscales are used in meso and macro scales without resort of empirical-adjustable parameters. Even these types of calculations can be defined *ab initio*. (De Luca et al. 2014) recently, have used different approaches, ranging from quantum mechanics to macroscopic models, to simulate the formation of the protein cake on a membrane surface and the consequent decay of water flux. Although various parameters were calculated *ab-initio* others have not yet been assessed in this way; however, this work represents one of the first attempts of an *ab-initio* simulation of a membrane process.

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Acetic Acid Dehydration by PV

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Acetic acid is an important organic chemical used in a wide range of applications worldwide. Among others, it is used as a raw material in the synthesis of vinyl acetate monomer (VAM) for the production of a wide variety of polymers. These include polyvinyl acetate, polyvinyl alcohol, polyacetals, and ethylene vinyl acetate copolymers (Minardi et al. 2002). A regular distillation process to dewater acetic acid is known to be energy intensive and to incur high operational costs. Since the separation of acetic acid from water using distillation is far from being the best process, any cost-efficient method to dehydrate acetic acid is in demand. Among these alternative methods, **pervaporation** has been suggested as a promising solution to separate acetic acid aqueous solutions (Algezhawi et al. 2005; Durmaz-Hilmioglu et al. 2001; Huang et al. 1988). Pervaporation is a membrane-based process that can be potentially applied to purify acetic acid (i.e., via **acetic acid dehydration**). It requires the availability of a system with a vacuum downstream to enable separation by partial vaporization through a dense, selective membrane. The permeation of a permeating component can be described in five consecutive steps: (1) sorption on the

membrane surface, (2) liquid diffusion through the membrane matrix, (3) vaporization, (4) vapor diffusion, and (5) vapor desorption (Van der Bruggen 2009). Several studies have been undertaken on dehydration of acetic acid-water mixtures using organic, inorganic, and composite membranes. It has been shown that inorganic membranes, in most cases, are capable to provide a very high selectivity of water, which penetrates through the membrane, but with a very low permeate flux, e.g., using zeolites. In an acid-proof silicalite-1 zeolite study, it was found that the separation factor was near infinite (Masuda et al. 2003). A study using free-radical graft polymerization of 1-vinylimidazole (VI) onto the as-synthesized mordenite zeolite membrane in acetic acid dehydration has been conducted by (Chen et al. 2010). It was found that by applying this membrane in pervaporation at higher temperature, it yields a higher flux and also a higher selectivity. Another interesting study was the investigation by Teli et al. (2007) on applying a silicotungstic acid incorporated sodium alginate (STA-NaAlg-5). This study gave an excellent separation factor and flux, ranging from 0.194 to 0.489 kg/m² h. However, the membrane performance decreased when applied at high temperature and in a more dilute feed solution. As the temperature and water content in the feed solution are increased, the flux increases and selectivity decreases. Other than inorganic membranes, polymeric membrane shows promising solution. Pervaporation up to 90 wt.% acetic acid using polyphenylsulfone membranes at temperature range from 30 to 80 °C exhibited high flux, good separation factor, and membrane stability (Jullok et al. 2011). The plasticizing effect was postulated to result in a special sieving property, which assisted the water molecules to be transported across the membrane matrix.

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Acetic Acid Dehydration by Pervaporation with Charged Membranes

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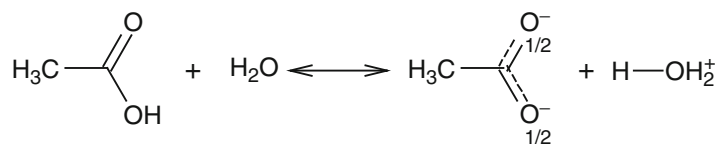
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Acetic acid is produced both synthetically and biologically. The synthetic production typically uses the Monsanto process, which is also known

as methanol carbonylation for acetic acid synthesis. About 75 % of acetic acid in the chemical industry is produced by this process, in which carbon monoxide reacts with methanol under influence of a rhodium complex catalyst at 180 °C and pressure of 30–40 atm (Shen et al. 2011). The main challenges in acetic acid and water separation are (1) cost minimization and (2) optimizing separation efficiency. In acetic acid aqueous solutions, there is a dynamic equilibrium between neutral molecules and the acetate and hydronium ions. It was observed that acetic acid dissociation is not only driven by the breaking of H-bonds connecting the ions but also triggered by a solvent reorganization around the proton-accepting water (Park et al. 2006), as illustrated in Scheme 1. Water molecule forms four hydrogen bonds, whereas a hydronium ion only forms three. Due to the proximity of the boiling point between acetic acid and water, separation using conventional methods may not be the best choice to consider. **Dehydration of acetic acid by pervaporation with charged membranes** can potentially be applied. Ion exchange membranes are pictured as porous with charges lining the pore walls. An example of ion exchange membrane used for this specific application is Nafion 117, which has been modified to form Nafion (C₈H₁₇)₄N⁺. Other ion exchange membranes which have been evaluated include sulfonated polysulfone (PSF(SO₃[−])-H⁺) and cross-linked styrene-co-butadiene base. They are mechanically stabilized with poly(vinyl chloride) baking and contain quaternary ammonium and sulfonic acid moieties, respectively (AMV-CH₃OO[−] and CMV-H⁺). The interaction of polymers with water is strongly influenced by the fixed ion and counterion. Hydrogen-bonding, dipole-dipole, and ion-dipole are the three possible interactions between water molecules and membrane surface. As the interaction between fixed ion and counterion with water increases, the sorption selectivity to water increases. A polymer having H⁺ as counterion has a lower water sorption and lower water sorption selectivity compared to a polymer having metal counterion. Besides, H⁺-containing polymer also has a high permeability but low separation factor. On the other hand, for a similar

Acetic Acid Dehydration by Pervaporation with Charged Membranes,

Scheme 1 Dissociation of acetic acid in water



polymer, which has a metal counterion, pervaporation shows lower permeability but higher separation factor (Semenova et al. 1997).

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Acetic Acid Dehydration by Pervaporation Zeolite Membranes

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The best performance in pervaporation for water dehydration corresponds to zeolite A, which is the zeolite with the lowest Si/Al ratio (equal to 1) and therefore the highest hydrophilicity. However, the high aluminum content of this zeolite makes it unstable under acidic conditions and it dissolves at low pH.

The separation of water in the presence of acetic acid or other acids could be important in the case of membrane reactors, active zeolite membrane reactors (AZMRs), for equilibrium displacement (see also Membrane reactor equilibrium conversion and Pervaporation membrane reactor). The esterification reaction using acid produces water that could be

removed continuously using a water permeable acid resistant membrane.

The most promising results concerning separations in acid medium have been obtained with zeolites with a moderate Si/Al ratio such as zeolite T with Si/Al = 4 or mordenite with Si/Al ratio from 7 to 20. Both zeolites have been tested in water/acetic acid mixture (50/50 wt.%) showing stability after the exposure to this mixture at mild temperature around 70 °C for several days.

Although the performance of these zeolites in pervaporation for water dehydration are lower compared to zeolite A (Arruebo et al. 2008), the acid stability of these zeolites is higher than that of zeolite A and makes them good candidates for the separation of acid mixtures. The researchers of Mitsubishi studied the technical feasibility of mordenite membranes for dehydration of acetic acid aqueous solution with a feed rate of 1000 kg h⁻¹. Their results suggested that the developed mordenite membrane deserved to the further technically developments of up-scale and mass-production (Sato et al. 2011). The membrane performance in pervaporation was measured in a feed mixture of water (50 wt.%) / AAc (50 wt.%) to be 10.9 kg m²/h for permeate flux and to be 0.77 × 10⁻⁶ mol m²/sPa for water permeance with separation factor of 500 at 130 °C.

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Acid Gas: Effect on Membrane Properties

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Acidic gas removal is the largest application of gas separation membranes and a vital process in the natural gas processing industry. Membranes used in this process are designed to separate H₂S and CO₂, and this process is known as natural gas sweetening. This is readily required for low-quality natural gas reserves, which need to be processed to achieve pipeline specifications of CO₂ <2 mol% and H₂S <4 ppm (Baker 2001). The removal of acidic gases is also required for biogas and gasification, where H₂S and CO₂ are separated from CH₄, CO, and H₂. For natural gas sweetening, the membrane must exhibit high permeability for H₂S and CO₂, with a large selectivity relative to methane.

In general, nonporous polymeric membranes are applied in acidic gas removal, taking advantage of the solution-diffusion mechanism and the high solubility of H₂S and CO₂, compared to CH₄. Also polymeric membranes almost always demonstrate selectivity for H₂S over CO₂, again because of the higher condensability of H₂S compared to CO₂, as demonstrated by the difference in critical temperature. Table 1 provides the H₂S permeability and H₂S/CO₂ selectivity for a range of polymeric membranes. The study of porous membranes for acidic gas removal is limited,

even though both H₂S and CO₂ have smaller kinetic diameters than CH₄. In the natural gas sweetening industry, both cellulose acetate- and polyimide-based membranes have been commercialized.

Prolonged exposure to both H₂S and CO₂ can lead to plasticization and degradation of the polymeric membrane over time. This is because the acidic nature of the gases means they will readily interact with the polymeric chains, disrupting chain packing and lubricating polymer chain motion, resulting in more rubbery behavior. Membrane degradation by these gases is greatly enhanced if water is present, because of the weak acidic dissociation of these gases (Scholes et al. 2009).

For inorganic and metallic membranes, H₂S is of particular concern, because of the effect sulfur can have on the membrane material (Lu et al. 2007). A good example of this is in H₂ separation with Pd-based membranes. The presence of H₂S leads to membrane brittleness and performance degradation because of lattice expansion on the formation of Pd-S. Hence, in applications such as gasification, it is necessary for the gas to have H₂S removed prior to the gas separation membrane, use sacrificial layers, or add sulfur-resistant materials.

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Acid Gas: Effect on Membrane Properties, Table 1 H₂S permeabilities (barrier) and H₂S/CO₂ selectivity in a range of polymeric membranes

	H ₂ S permeability	H ₂ S/CO ₂
Ethyl cellulose	320	3.8
Nylon	0.34	3.86
PDMS	5,100	1.6
Polyethylene	36	2.84
PTMSP	21,400	1.2

A-CNT

► [Aligned Carbon Nanotube](#)

Activity Coefficient

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Chemical Thermodynamics

Depending on a specific area of fundamental science and technology, the term “activity” may have a different meaning. For example, in chemical thermodynamics, activity (a) is well known as a convenient variable to represent data, obtained experimentally or calculated theoretically, for the values of chemical potentials of components in real chemical solutions. For the i – th component of a mixture, activity a_i is defined as follows: $\mu_i = \mu_i^0 + RT\ln(a_i)$, where μ_i is the chemical potential of a component and μ_i^0 is the chemical potential of that component in standard state. R is the gas constant and T is the thermodynamic temperature. The numerical value of the activity depends on the choice of a standard state, as it describes the difference between an actual chemical potential and a standard chemical potential.

Fuel Cells and Electrocatalysis

In hydrogen fuel cell science and technology, activity is often referred to as the measure of efficiency of electrocatalysts. Electrocatalytic processes in fuel cells occur on the surface of electrodes, and one of the main challenges is to explain, predict, and improve electrocatalytic activity of various electrode materials. In the area of low temperature PEM (proton exchange membrane, also called polymer electrolyte membrane) fuel cells, catalytic activity is often used to compare efficiency of electrocatalysts toward kinetics of the oxygen reduction reaction (ORR) occurring at the cathode. ORR is known to have slow kinetics due to the reaction having multiple steps and difficulties in breaking the O–O bond, which leads to a larger

cathodic overpotential (Zhang 2008). In this case, overpotential is defined as the extra potential over the equilibrium value that must be applied to cause an electrode reaction at a certain rate. Thus, an electrocatalyst with high activity is required to minimize the overpotential.

According to the Sabatier principle (Bligaard et al. 2004), a volcano-shaped curve is obtained when the activity of a catalyst for ORR is plotted as a function of a variable that relates to the ability of the electrocatalyst surface to form chemical bonds with oxygen, reaction intermediates, and/or products (Nørskov et al. 2004). For example, it was shown that the catalytic activity of a single Pt-based electrocatalyst toward ORR depends strongly on such variables as the O₂ adsorption energy, the dissociation energy of the O–O bond, and the binding energy of OH on the catalyst surface. The electronic structure of the Pt catalyst (Pt d-band vacancy) and the Pt–Pt interatomic distance (geometric effect) can strongly affect these variables. Theoretical calculations on O₂ and OH binding energy on several metals have predicted that Pt should have the highest electrocatalytic activity among other metals with the ORR activity of Pt > Pd > Ir > Rh, which is in agreement with experimental results. Calculations have also predicted that Pt–M (M = Fe, Co, Ni, etc.) bimetallic alloys should have higher catalytic activity than pure Pt, which has again been proven by experiments (Nørskov et al. 2004).

Practical Measurements

Practically, electrocatalytic activity of various electrocatalysts can be compared by measuring electrical currents produced at a given overpotential. The electrocatalyst that generates higher current at lower overpotential is generally a better electrocatalyst.

The rotating disk electrode (RDE) technique is often used to measure ORR activity of electrocatalysts for hydrogen PEM fuel cell applications. Typically, current density j is measured at 0.9 V at the positive voltage sweep at a certain electrode rotating speed. The measured current

density j is expressed by the following equation: $\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} + \frac{1}{j_f}$, where j_k is kinetic current density, j_d is hydrodynamic diffusion limiting current density, and j_f is film diffusion limiting current density. RDE experiments should be designed to maximize j_f . In that case, $\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}$ and after rearrangement $j_k = j \times j_d / (j_d - j)$.

For ORR the value of j_d is normally taken at 0.4 V during RDE experiments.

Once j_k is known, activity is often reported in practical values as mass activity (A/mg Pt) by normalization to the value of Pt loading of the sample on the disk electrode.

Another practically important way of reporting the electrocatalyst activity is to use area-specific activity. The area-specific activity, expressed in the following units, $\mu\text{A}/\text{cm}^2$ Pt, is reported by normalization of j_k to the electrochemical surface area (ECSA) of the catalyst.

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Acute Kidney Injury (AKI)

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Synonyms

Membrane artificial organs

Acute kidney injury (AKI) or acute renal failure indicates kidney injury from less severe forms of injury to more advanced injury when acute kidney failure may require renal replacement therapy. Acute kidney failure occurs when kidneys lose their functions that include excretion of wastes, acid-base homeostasis, osmolality regulation, blood pressure regulation, and hormone secretion (Waikar et al. 2008). When kidneys lose their filtering ability, dangerous levels of wastes may accumulate, resulting in an increasingly toxic blood stream and fluid overload. Acute kidney failure requires replacement therapy that includes: hemodialysis, peritoneal dialysis, hemofiltration, hemodiafiltration, and renal transplantation. Dialysis treatment involves the diffusion of solutes through a semipermeable membrane driven by a concentration gradient. For the treatment of uremic patients, an artificial membrane (hemodialysis) or a biological membrane (peritoneal dialysis) can be utilized. The membrane-based treatments involve pumping patient's blood from the body through a membrane device that acts as an artificial kidney by separating waste products including toxins and excess water from the blood. The therapies for the treatment of patients with acute renal failure are not limited to dialysis but rather include other modalities. Hemofiltration has been developed to overcome the reduced efficacy of diffusion for molecules with middle and large MW. In this process the driving force is a hydrostatic pressure gradient that induces a large flux of water across the membrane from blood side to the filtrate side. As a result the rate of solute removal is proportional to the applied pressure. Hemodiafiltration is the combination of hemodialysis and hemofiltration processes. The high rate of ultrafiltration is combined with the efficient diffusion overcoming the disadvantages related to each single treatment.

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Addition Norbornene Polymer-Based Membrane Materials

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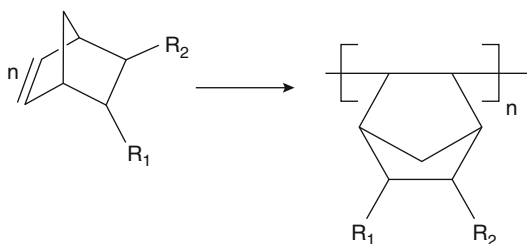
Substituted norbornenes and tricyclononenes can be polymerized according to the addition scheme, that is, via opening of the double bonds of these cycloolefins (Finkelshtein et al. 2011; Yampolskii 2010).

The resulting glassy polymers have very rigid main chains and high glass transition temperatures. The gas permeation parameters of the obtained polymers strongly depend on the substituents in the monomer molecules. Thus, nonsubstituted addition polynorbornene (PNB) is a relatively low-permeability polymer ($P(\text{O}_2) = 11$ Barrer), though when substituents are introduced permeability increases markedly (Fig. 1). In particular, methyl-substituted PNB has $P(\text{O}_2) = 89$ Barrer, while for the polymer with bulkier, SiMe_3 substituent, the permeability is further strongly enhanced ($P(\text{O}_2) = 980$ Barrer) (Yampolskii 2010). SiMe_3 -substituted PNB and poly(tricyclononenes) reveal large free volume according to the positron annihilation lifetime spectroscopy and solubility-controlled selectivity in separation of hydrocarbons (Finkelshtein et al. 2011; Gringolts

et al. 2010): permeability coefficients increase for penetrants with larger size or molecular mass (e.g., butane). This makes them important candidates for membranes for separation of natural and associated petroleum gas, especially because their gas permeation parameters are relatively stable in time in comparison with highly permeable polyacetylenes. These polymers are soluble in various organic solvents, so high-flux composite membranes (permeance of about $5\text{--}15 \text{ m}^3(\text{STP})/\text{m}^2 \text{ h bar}$) can be prepared from them.

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Addition Norbornene Polymer-Based Membrane Materials, Fig. 1 Addition Norbornene Polymer-based Membrane Materials

Adhesion to Membrane Surfaces

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Adhesion to membrane surfaces generally describes the sticking or holding fast of some substances such as paints, cells, platelets, bacteria, proteins, etc. on membrane surfaces when they are in contact. Usually, the intermolecular interaction is responsible for the adhesion of substances on membrane surfaces (Huang et al. 1999). The

adhesion can be divided into several categories, including mechanical adhesion, chemical adhesion, dispersive adhesion, electrostatic adhesion, and diffusive adhesion according to the forces that cause adhesion. The adhesion is a stronger interaction between unlike substances than adsorption (Jacek et al. 1999). In the filtration operation using a membrane, the adsorption and adhesion of foulants such as colloids, particles, proteins, bacteria, and microorganisms on membrane surfaces result often in membrane fouling that induces the severe flux loss and the increase of transmembrane pressure. Membrane fouling can be divided into reversible fouling and irreversible fouling. Reversible fouling is often attributed to the adsorption of foulants on membrane surface, and it can be recovered by physical or chemical membrane cleaning. While irreversible fouling is usually generated from the firm adhesion of foulants on membrane surface, and it is difficult to be removed even if a thorough membrane cleaning is done (Jonathan and Amy 2004). Therefore, the adhesion of foulants on membrane surface often brings a permanent deterioration of membrane performance. In such a case, the fouled membrane modules have to be replaced to continue a normal filtration operation.

In blood-contact membrane separation, for the blood incompatible membrane materials, the platelets in blood tend to accumulate and adhere onto membrane surface due to a biological immune reaction. As a result, thrombus formation may form and further result in some serious complications. Therefore, the blood-contact membranes such as hemodialysis membranes often need be modified to prevent the adhesion of platelets on membrane surface during blood filtration. In membrane science, the experiment of platelet adhesion on membrane surface is usually employed to evaluate the hemocompatibility of a blood-contact membrane. In biomedical application, the adhesion of microbes on membrane surface often leads to the bacterial infection of patients and the deterioration of membrane materials. Therefore, the control of microbial infection is a very important issue in biomedical membrane separation.

Cross-References

- [Adsorption onto Membrane Surfaces](#)
- [Bioadhesion to Membrane Surface](#)

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Adsorption onto Membrane Surfaces

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Adsorption onto membrane surface is the accumulation of gases, liquids, or solutes to form a thin film on membrane surface. In adsorption, the adsorbate is attracted to the surface of adsorbent, but does not enter its molecular spaces. As a surface phenomenon, adsorption is a consequence of surface energy. Adsorption is similar to adhesion and absorption, but there exist differences between them. Generally, compared to adhesion, adsorption is looser interaction between unlike substances. Adsorption is a surface-based process, while absorption involves the whole volume of the material. The exact bonding nature of adsorption depends on the details of the species involved, but the adsorption process is generally classified as physical adsorption and chemical adsorption. The physical adsorption is attributed to the non-covalent interaction such as van der

Waals force, electrostatic attraction, etc. The chemical adsorption features the formation of covalent bonding between adsorbate and adsorbent (Ferrari et al. 2010).

Commonly, in liquid filtration using a membrane, adsorptions onto membrane surface describe the accumulation and attachment of solutes in liquid on membrane surface driven by the minimization of interfacial energy. In water phase filtration, the adsorption of foulants such as proteins, colloids, microorganisms, etc., on membrane surfaces and membrane pore walls is often responsible to membrane fouling that induces a severe loss of membrane permeability and a change in membrane separation characteristics. The adsorption of foulants can be removed (desorption) by chemical or physical washing if the interaction between foulants and surfaces is weak. As a result, the membrane performances can be recovered partially or fully. In blood-contact membrane separation, protein adsorption on membrane surface often leads to the activation of complement system and blood coagulation and further results in serious complications of patients. Protein adsorption onto membrane surface is influenced by the surface characteristics such as wettability, surface chemistry, morphology, surface charge, etc. Therefore, surface modification of the blood-contact membranes to depress the adsorption of proteins on membrane surface has been a pursuit of membrane researchers (Rana and Matsuura 2010).

Cross-References

► [Adhesion to Membrane Surfaces](#)

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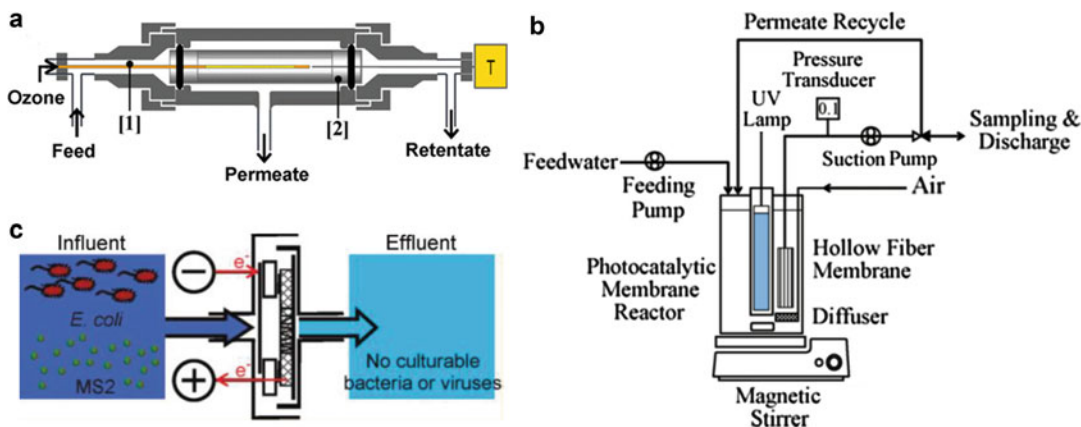
Advanced Oxidation Process (AOP) by Membrane Reactors

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Advanced oxidation process (AOP) by membrane reactors is a synergistic hybrid of hydroxyl radical reaction and membrane filtration in a single reactor. Advanced oxidation process (AOP) is the uncontrolled, destructive action of hydroxyl radicals generated from ozone, H_2O_2 , ultraviolet radiation, Fenton reaction, electrolysis, sonolysis, and photocatalysis (e.g., TiO_2). AOP is most widely used for the decomposition of nonbiodegradable organic contaminants present in industrial and municipal wastewaters. It can be also applied for the degradation of micro-contaminants and taste-and-odor causing compounds in drinking water sources, such as pesticides, pharmaceuticals, endocrine disruptors, microcystins, geosmin, etc. Although micro-/ultrafiltration membranes are almost complete barriers for particulate matter and pathogens in water, they are limited in removing dissolved organic compounds. Thus, the coupling of membrane filtration with AOP in a reactor provides multifunctionalities and flexibilities for water and wastewater treatment systems.

Advanced oxidative membrane reactors are similar to biological membrane reactors (i.e., membrane bioreactors) in their concept except that biological oxidation is replaced by chemical oxidation. Due to the incompatibility of hydroxyl radicals and membrane materials (e.g., polymeric membranes), however, only a few examples of process configurations are developed and introduced, such as ozonated membrane reactor (Heng et al. 2007), photocatalytic membrane reactor (Choo et al. 2008), and electrochemically active filtration device (Vecitis et al. 2011). Figure 1 shows the schematics of such advanced oxidative membrane reactors. The ozone membrane reactor consists of ceramic tubular membranes made of alumina and zeolite which are chemically durable



Advanced Oxidation Process (AOP) by Membrane Reactors, Fig. 1 Examples of advanced oxidative membrane reactors: (a) ozone membrane reactor (Heng et al.

2007), (b) photocatalytic membrane reactor (Choo et al. 2008), and (c) electrochemically active filtration device (Vecitis et al. 2011)

while degrading a fraction of total organic carbon by ozone. The photocatalytic membrane reactor with suspended TiO_2 particles in aqueous phase enables polymeric membranes to be used because photocatalysis only occurs on the surface of TiO_2 photocatalysts where UV light bombards. The membrane permeability is enhanced with continuous photocatalysis of organic substances; otherwise they can foul the membrane severely. The fabrication and use of TiO_2 membranes for photocatalytic membrane reactors are of great interest, but UV light radiation is a major hurdle to be resolved. When a direct current of 2–3 V was applied onto multiwall carbon nanotubes loaded on a 5- μm polytetrafluoroethylene filter, substantial viral and bacterial removals are achieved by electrolysis in addition to filtration. Further process developments on AOP membrane reactors are expected with novel membrane materials and process designs.

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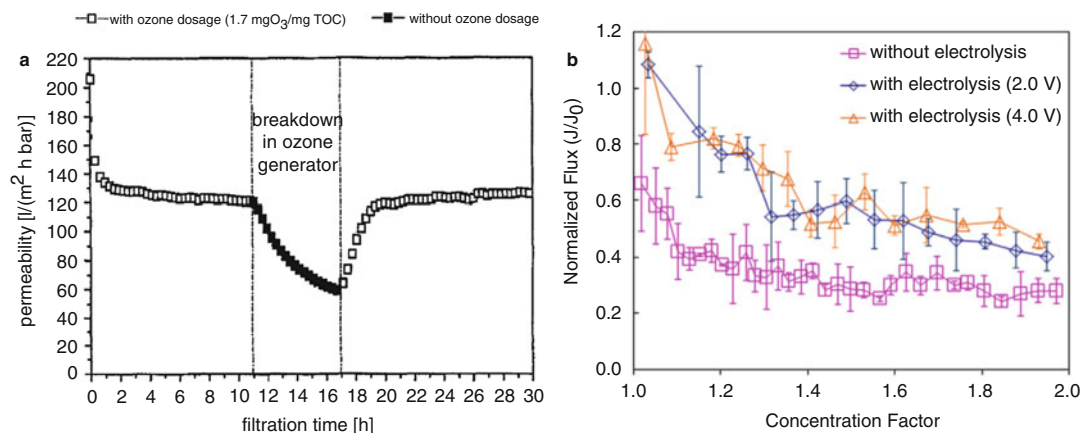
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Advanced Oxidation Processes (AOPs) and Membrane Operations

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Advanced oxidation processes (AOPs) and membrane operations are composed of advanced oxidation followed by membrane filtration, where the former decomposes dissolved organic matter and the latter removes particulate matter. Advanced oxidation process (AOP) is the uncontrolled, destructive action of hydroxyl radicals generated from ozone, H_2O_2 , ultraviolet radiation, Fenton reaction, electrolysis, sonolysis, and photocatalysis (e.g., TiO_2). AOP is most widely used for the decomposition of nonbiodegradable organic contaminants present in industrial and municipal wastewaters. It can be also applied for the degradation of micro-contaminants and



Advanced Oxidation Processes (AOPs) and Membrane Operations, Fig. 1 Membrane flux enhancement with advanced oxidation pretreatments: (a)

ozonation plus ultrafiltration (Schlichter et al. 2004); (b) electrolysis plus microfiltration (Park et al. 2013)

taste- and odor-causing compounds in drinking water sources, such as pesticide, pharmaceuticals, endocrine disruptors, microcystins, geosmin, etc. This combined process can compensate the weak point of each process, but the oxidants left over should be quenched before their contact with polymeric membranes. This is because oxidants can deteriorate the membrane lifetime or integrity significantly due to the oxidation of the membrane. Polyamide membranes can be damaged even by the attack of chlorine and thereby, their physical properties and filtration performance are significantly impaired. Reducing agents, such as sodium sulfite, are mostly used for oxidant quenching.

A series of oxidation (e.g., ozonation) and micro-/ultrafiltration processes are designed and used for the treatment of drinking water which contains trace organic contaminants as well as metal species (e.g., Fe^{2+} , Mn^{2+}) (Hyung et al. 2000; Choo et al. 2005). Ozone can facilitate the oxidation of reduced forms of such metal ions and so help to precipitate out. The precipitates can be readily rejected by porous membranes. Electrolysis in combination with microfiltration is developed and tested for the treatment of municipal wastewater organic matter with simultaneous hydrogen production (Park et al. 2013). Electrochemical oxidation at a voltage of >2.3 V enables hydroxyl radicals to be generated while oxidizing

and ultimately mineralizing organic matter. Membrane operations after electrolysis achieve further removal of particles that can be hardly oxidized. A process configuration that consists of advanced oxidation (e.g., Fenton oxidation) followed by a membrane bioreactor is also an attractive option for the treatment of industrial wastewater containing recalcitrant organic chemicals (e.g., dyes) (Feng et al. 2010). This combination can be applied for the minimization of biological sludge generation while disintegrating excessive activated sludge (He and Wei 2010). To take advantage of prolonged oxidation, inorganic membranes (e.g., ZrO_2 and Al_2O_3 membranes), which are tolerant to strong oxidants, can be used instead of polymeric membranes. Particularly, advanced oxidation treatment prior to membrane filtration helps to reduce membrane fouling caused by organic substances (Fig. 1) (Park et al. 2013; Park 2002; Schlichter et al. 2004).

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Aerobic Membrane Bioreactor

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Synonyms

Cross-flow membrane bioreactor; Membrane bioreactor; Microfiltration membrane bioreactor; Submerged membrane bioreactor; Ultrafiltration membrane bioreactor

Introduction

Aerobic membrane bioreactors (MBRs) are one of the leading technologies to achieve sustainability in wastewater treatment through reuse, decentralization, and low energy consumption (Fane and Fane 2005; Fawehinmi et al. 2005). In aerobic MBRs, aerated activated sludge is coupled with membrane process to remove dissolved

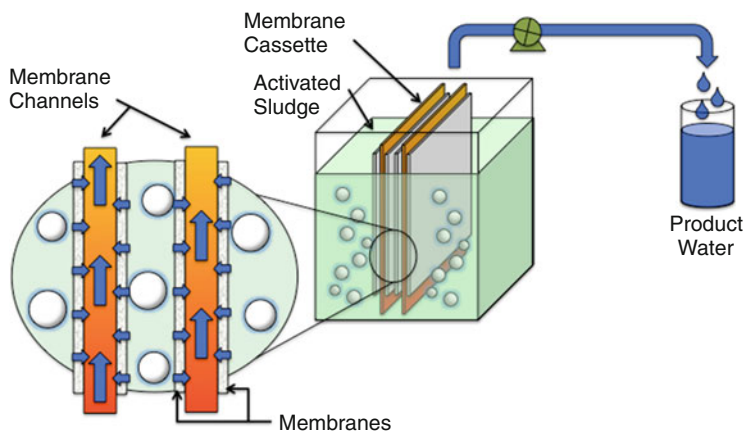
contaminants (carbon and ammonia) and separate solids from the treated municipal or industrial wastewater. Carbon is removed by microorganisms that metabolize the carbon in the presence of dissolved oxygen for microbial growth and respiration (organic carbon reduced to carbon dioxide). Ammonia is removed through ammonia oxidation (nitrification). Nitrification is a microbially mitigated reduction process that occurs in an aquatic environment that contains moderate to high concentrations of ammonia and dissolved oxygen and low concentrations of organic carbon.

In submerged MBRs (Fig. 1), microporous (microfiltration (MF) or ultrafiltration (UF) (► [Ultrafiltration](#))) membranes are immersed in a bioreactor, and water is filtered (► [Permeate](#)) through the membranes using vacuum; suspended solids are retained in the system; and high levels of treatment (including nutrient removal) can be achieved (Judd 2006). The MBR replaces the two-stage conventional activated sludge process (biotreatment and clarification) with a single, integrated process (► [Wastewater Treatment in Membrane Bioreactors](#)). The advantages of MBRs over conventional treatment have been thoroughly reviewed (Stephenson et al. 2000), and they include product consistency, reduced footprint, reduced sludge production, and nearly complete suspended solid separation from the effluent. Additionally, MBR effluent may be suitable for use as irrigation water, as process water, or as a pretreatment for potable reuse applications (Membrane Bioreactors for Reuse; Potable Water Production) (Lawrence et al. 2002).

However, the establishment of membrane bioreactor technology (Anaerobic Membrane Bioreactor; Attached Growth Membrane Bioreactor; Membrane Bioreactors (MBR) for Plants; ► [Submerged Membrane Bioreactor](#)) has been slower than expected because decision-makers view MBRs as high risk and costly compared to conventional technology (Judd 2006). To date, MBRs have been used to treat municipal and industrial wastewater where water reuse is desired, a small footprint is required, or stringent discharge standards exist (Kang et al. 2007; Yang et al. 2006).

Aerobic Membrane Bioreactor,

Fig. 1 Schematic representation of a submerged aerobic MBR system



Current Limitations

One of the major limitations to widespread application of MBR technologies is to control membrane fouling with modest energy and chemical input (► [Irreversible Fouling](#); ► [Reversible Fouling](#)) (Le-Clech et al. 2006). Membrane fouling (Biological Fouling; Cake Layer; ► [Inorganic Scaling](#)) has been investigated from various perspectives, including the causes, characteristics, and mechanisms of fouling and methods, to prevent or reduce membrane fouling (Achilli et al. 2011; Judd 2005; Le-Clech et al. 2006; Meng et al. 2009; Wang and Wu 2009). Fouling markedly affects membrane cleaning (Membrane cleaning, 369690) and replacement intervals, system productivity, and membrane integrity; all of which are factors that affect energy requirements and costs (Judd 2006; Le-Clech et al. 2006).

Operation

In order to operate conventional MBRs at constant flux, physical membrane-cleaning techniques are utilized; they include air scouring, backwashing, relaxation, or a combination of the three, depending on the membrane configuration (hollow fibers, flat sheet, or tubular). Air scouring is required for submerged MBR configurations to gas lift fresh sludge through the membrane bundle or cassette and to scour solids from the membrane surface. During backwashing, permeate is

pumped in the opposite direction through the membrane, effectively removing most of the reversible fouling (► [Backwashing](#)). The efficiency of backwashing has been studied in detail, and the key parameters have been found to be frequency, duration, and intensity (► [Backwashing Frequency](#)) (Bouhabila et al. 2001; Psoch and Schiewer 2005, 2006). During membrane relaxation, permeate suction is stopped, and the back transport of foulants is naturally enhanced as reversibly attached foulants diffuse away from the membrane surface.

Membrane backwashing and relaxation are regularly used for tubular and hollow fiber membranes to control fouling (Bouhabila et al. 2001; Hong et al. 2002; Psoch and Schiewer 2005, 2006; Smith et al. 2005). This is not the case for flat-sheet membranes that cannot be backwashed due to their inability to withstand pressure in the opposite direction of the operating flow; for this reason, relaxation is used to control the fouling of these membranes (Le-Clech et al. 2006). Regardless of the membrane configuration, chemicals must be used at regular intervals to enhance physical cleaning (Le-Clech et al. 2005).

Cross-References

- [Backwashing](#)
- [Backwashing Frequency](#)
- [Industrial/Tannery Wastewater Treatment Using Membrane Bioreactors](#)

- Inorganic Scaling
- Irreversible Fouling
- Permeate
- Reversible Fouling
- Submerged Membrane Bioreactor
- Ultrafiltration (UF)

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Affinity Membranes

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Introduction

Affinity separation methods rely on a “molecular recognition” phenomenon between species. A molecule, known as the ligand, is permanently bounded onto an inert matrix and specifically recognizes the molecule of interest, known as the ligate, that can be separated. The ligand can be a naturally occurring molecule, an engineered macromolecule, or a synthetic molecule linked to the matrix by covalent coupling. The ligand-ligate interaction is selective and reversible, enabling the separation and fine purification of biological substances such as proteins, peptides, and nucleic acids on the basis of its individual chemical structure or biological function (Wilson and Poole 2009).

Among the separation techniques based on the affinity method, affinity chromatography is the most widely used. Due to the limitation associated to the traditional affinity chromatography with porous bead-packed columns (i.e., limited flow rate by pore diffusion), the membrane-based separation technique is gaining an increasing

importance. Indeed, affinity membranes combine the specificity of affinity adsorption (of the common affinity resins) with the high productivity associated with filtration membranes. They provide low pressure separation systems without diffusional limitation, as the mass transfer is mainly governed by convection (Klein 2000). Microporous membranes, both in flat sheet and hollow fiber configuration, coupled with biological or biomimetic ligands have been used as affinity membrane chromatography supports (Zou et al. 2001).

Affinity Membrane Preparation

The realization of affinity membranes usually involves three steps: (1) preparation of the basic membrane, (2) activation (functionalization) of the basic membrane, and (3) coupling of affinity ligands to the activated membrane.

Membrane Material

The membrane materials should possess some characteristics: (i) hydrophilicity to minimize the nonspecific adsorption of bioactive species, (ii) chemical and physical stability under harsh conditions used during ligand coupling and ligand-ligate complex formation, (iii) large surface area relative to membrane volume, (iv) biocompatibility when the membrane is used for blood treatment, and (v) presence of functional groups required for the coupling of the ligands (such as $-\text{OH}$, $-\text{NH}$, $-\text{SH}$, $-\text{COOH}$).

The commercially available materials used for affinity membrane preparation include organic (natural or synthetic polymer), inorganic, and composite materials.

Among the first materials used for affinity membrane preparation, cellulose and its derivatives (regenerated cellulose, cellulose acetate) were the most common. These present a hydrophilic and biocompatible surface, low nonspecific adsorption, and abundant reactive hydroxyl groups that can be easily activated by different strategies for the ligand coupling. To improve the

density of functional groups and increase the mechanical strength, composite cellulose membranes have been also prepared by chemical grafting with acrylic polymers.

Another suitable membrane material is polyvinyl alcohol, thanks to its hydrophilicity and biocompatibility. Like cellulose, it contains hydroxyl groups that can be easily activated.

Polyamide and nylon have been also used for the preparation of affinity membranes, thanks to their good mechanical and chemical stability. Nylon membranes have a low concentration of amino groups to serve as functional groups for ligand coupling. Also, due to the hydrophobic surface, the membrane presents a high nonspecific adsorption of biomolecules during affinity separation process. Therefore, the hydrolysis of the membrane is generally performed to increase the density of reactive groups and to prevent electrostatic interaction with proteins. To overcome these problems, composite nylon membranes have been also prepared.

Other materials that have been used for affinity membranes are poly(methyl methacrylate), polysulfone and its derivative, polycaprolactam, polyvinylidene difluoride, poly(ether-urethane-urea), and inorganic materials such as glass.

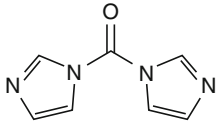
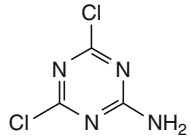
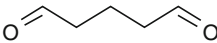
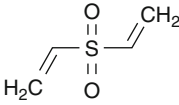
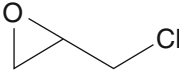
Membrane Activation and Ligand Coupling

If the basic membrane does not possess the functional groups for ligand coupling, it can be activated.

In Table 1 are reported the commonly used activation agents with respect to the functional groups present on the basic membrane.

The coupling of the ligand directly on the activated membranes may result in low binding specificity due to the low steric availability (in particular when the ligand is a small molecule). This problem is generally overcome by the introduction of a spacer molecule to the membrane prior to attaching the ligand, improving the ligand accessibility for the molecule to be separated. Spacer arms are bifunctional molecules able to react with both the membrane and ligand.

Affinity Membranes, Table 1 Some commonly used activation agents for affinity membrane preparation

Activation agent	Structure	Functional groups of the basic membrane
Cyanogen bromide	$\text{N}\equiv\text{C}-\text{Br}$	-OH
Carbonyldiimidazole		-OH, -NH ₂
2-Amino-4,6-trichloro-s-triazine		-OH
Glutaraldehyde		-OH, -SH, -NH ₂
Divinyl sulfone		-OH, -SH
Epichlorohydrin		-OH, NH ₂

Affinity Ligands

Affinity ligands can be classified into biospecific and pseudo-biospecific ligands (Klein 1991). Biospecific ligands are biomolecules such as antibodies, antigens, and proteins A and G that show specificity for only one complementary biomolecule.

Because of their selectivity, biomolecules have been the most widely used affinity ligands on affinity membrane separation technology. One of the most common applications is the use of immobilized monoclonal antibodies for immunoaffinity separation. Another important example is membranes with covalently coupled protein A or protein G for immunoglobulin purification from plasma, serum, or cell culture supernatants.

Although the biospecific ligands possess high specificity for proteins, they have some limitation for large-scale application due to their poor stability and high price.

The alternative approach to biospecific ligands involves the use of pseudo-biospecific ligands. These are usually molecules with higher chemical and physical stability than biomolecules. Pseudo-biospecific ligands can be distinguished by biological (amino acids, specially histidine, lysine, tryptophan) or non-biological molecules (dyes, chelated metal ions).

The working principle of pseudo-biospecific ligands relies on the complementarity of structural features of ligand and ligate rather than on a biological function. Immobilized dyes have been found to act as affinity ligands for a wide variety of biological molecules. For example,

Affinity Membranes, Table 2 Some examples of the use of affinity membranes for isolation and purification of biomolecules

Membrane	Ligand	Ligate	Application
Cellulose and regenerated cellulose	Cibacron Blue F3GA	Alkaline phosphatase	Purification
	Protein A/G	IgG	Purification
	Histidine	Endotoxin	Removal of endotoxin
Poly(ethylene-co-vinyl alcohol)	Histidine	IgG	Purification
Nylon	Cibacron Blue	Glucose-6-phosphate dehydrogenase	Purification
	Protein G	IgG	Purification
	Histidine	Endotoxin	Removal of endotoxin
Polyvinylidene difluoride (PVDF)	Protein A	IgG	Purification
Polysulfone (PS)	Trypsin	Trypsin inhibitor	Purification
	Iminodiacetic acid (IDA)	Histidine/tryptophan	Purification
Glass	IDA-Cu ²⁺	Lysozyme, cytochrome c, ribonuclease A	Purification

triazine-linked dyes have been used to mimic coenzymes that bind a number of dehydrogenases, hexokinases, and alkaline phosphatases; the reactive triazine groups can be linked to any matrix containing hydroxyl groups by mixing the two together. Cibacron Blue F3GA (a textile dye) has been employed as ligand in affinity membranes for the purification of over 80 enzymes and proteins.

Another important example of pseudo-biospecific affinity ligands is chelated metal ions used for the purification of histidine-tagged fusion proteins.

Molecular Imprinted Membranes

A different approach for the preparation of affinity membranes is the use of molecularly imprinted polymeric materials. These are produced by entrapping a template molecule (the molecule to be separated) in a polymer matrix during polymerization and subsequent extraction. In this way, binding sites are introduced in the polymer that

are complementary in shape and functionality to the target molecule.

Applications of Affinity Membranes

Affinity membranes are used for several different applications such as purification of biomolecules, removal of unwanted substances from biological fluids, and also small-scale analytical separations.

The most common application is the separation and purification of biomolecules and especially proteins for large-scale production.

In Table 2 are reported some typical examples of their use for the separation and purification of biomolecules.

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Affinity Membranes for Adsorptive Separation Process

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Affinity membrane (also called *adsorptive membrane*, *membrane adsorber*, or *membrane chromatography*) is a design using membrane for adsorptive separation. The traditional shape for adsorbents is particle. In batch process, particulate adsorbents need to be suspended uniformly in liquid bath by agitation for good contact with adsorbates. After adsorption, centrifugation/filtration/precipitation is required to separate solid particles from the liquid. On the other hand, particulate adsorbents are commonly packed in a column/vessel (so-called *chromatography* or *packed bed*) for flow operation, where various operational conditions (fixed bed, moving bed, fluidized bed, etc.) could be applied. However, pressure drop and intraparticle diffusion limitations usually restrict the separation effectiveness of large-scale chromatographic system. An advantageous alternative for adsorptive separation is to adopt porous membrane with suitable functionality (adsorptive membrane), which has exhibited better mass transfer effects by convective transport of solutes and minimal thickness to allow operation at low pressure (Roper and Lightfoot 1995; Charcosset 1998; Zou et al. 2001; Ghosh 2002; Suen et al. 2003).

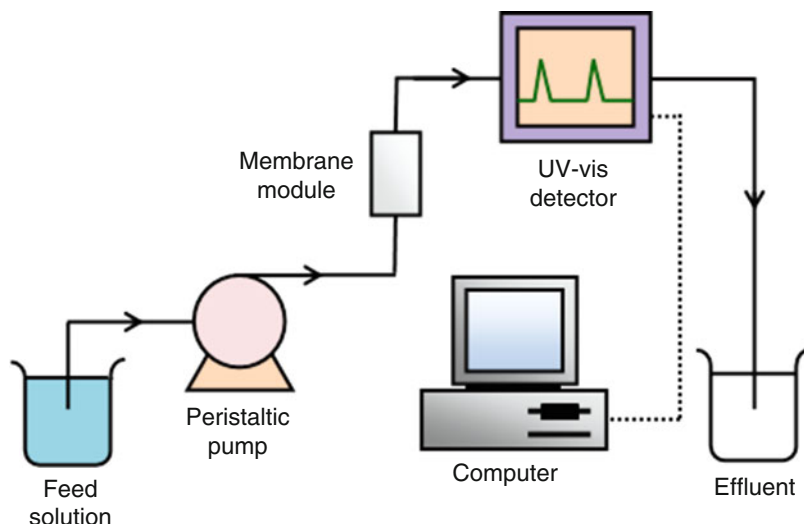
Adsorptive membranes are mainly applied in separation of biomolecules (proteins, DNA, endotoxins, etc.). Their application has been extended to the removal of toxic contaminants from wastewater (Wu et al. 2008). The interactions between adsorbates and adsorptive membranes are identical to those using particulate adsorbents. They could be categorized into four modes: affinity, ion exchange, hydrophobic interaction, and reverse phase (Roper and Lightfoot 1995; Charcosset 1998). Affinity mode provides strong specific binding, such as biospecific, immunoaffinity, dye affinity, immobilized metal ion affinity, and pseudo affinity. Ion exchange adsorption, including weak and strong, cation and anion exchange, is based on electrostatic interaction so that fast binding and high recovery are easily attained to increase its popularity in commercial products. The last two modes are both induced by van der Waals force and hydrophobic interaction, with a difference that the strength of reverse phase mode is larger. The applications of these two modes are limited due to the probable inactivation of biomolecules.

Several methods could be employed to prepare the adsorptive membranes: (1) polymerization of monomers containing special functional groups (or *ligands*), followed by dissolving of polymer and casting it into a film; (2) introduction of functional groups into a polymer in solution and casting it into a film; (3) immobilization of functional groups onto a preformed membrane; and (4) blending of particulate adsorbents and polymer solution together and casting it into a film (so-called *mixed matrix membrane*) (Avramescu et al. 2003; Saufi and Fee 2009).

Adsorptive membrane system can be operated using commercially available geometries such as flat sheet, tubular/hollow fiber, spiral wound, etc. (Roper and Lightfoot 1995; Zou et al. 2001; Suen et al. 2003). Figure 1 depicts the flow process of adsorptive membrane (i.e., membrane chromatographic system). Similar to a conventional chromatographic system with particulate adsorbents, a cycle of operation consists of

Affinity Membranes for Adsorptive

Separation Process,
Fig. 1 Schematic diagram
 of flow process for
 adsorptive membrane



loading (adsorption), washing, elution (desorption), and/or regeneration. To achieve a larger-scale adsorptive capacity, it is simple and convenient to stack flat sheet membranes in series or wind a larger sheet around a cylindrical core.

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Affinity Membranes for Purification of Enzymes

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Enzymes and Their Purification

Enzymes are large biological molecules that catalyze chemical interconversions. Most enzymes are proteins and they are highly selective catalysts. Since enzymes are selective for their substrates and speed up only specific reactions from among many possibilities, the types of enzymes determine the pathways and therefore affect the products of reactions. Hence, there is always the need for enzymes of different types to be separated and purified.

Affinity Membranes

Conventional membranes generally act like a sieve for separation, blocking substances larger than the membrane pores and passing substances smaller than the membrane pores. However, affinity membranes operate not only on the sieving mechanism but more importantly have

selective binding capabilities, provided by various binding sites on the external and internal surfaces of the membranes. Thus, affinity membranes can separate and purify substances with the combined advantages of high selectivity due to the specific binding sites and the high productivity of conventional filtration membranes.

Many affinity membranes were developed by postmodifications of existing microporous ultrafiltration and microfiltration membranes. Due to the different membrane materials, various modification approaches may have to be used to provide the specific binding sites on the membranes. For example, polymeric membrane materials with functional end-groups can directly react with reactive ligands. On the other hand, inert membrane materials, such as aliphatic hydrocarbons without active side chains or end-groups, are usually modified by radiation chemistry to incur their reactivity for ligand immobilization. Premodification of membrane materials may be another route to prepare affinity membrane. Functional monomers with binding sites were polymerized to have functionalized polymers that are subsequently used to fabricate affinity membranes.

The applications of affinity membranes are similar to those of affinity chromatography developed with the bead columns, but affinity membranes have the advantage of shorter process time, increased separation efficiency at low pressures, and greater productivity.

Purification of Enzymes with Affinity Membranes

One of the most important applications of affinity membrane is in purification of proteins or enzymes. The affinity membranes will trap or adsorb specific proteins or enzymes during the filtration of their solutions. The trapped proteins or enzymes are subsequently eluted from the membranes and concentrated to get the purified products. In general, there are three types of interactions between the affinity membranes and the enzymes. The first type of interaction is electrostatic interaction. Anions or cations are covalently immobilized onto the membranes to trap

positively charged or negatively charged enzymes, respectively. For example, porous nylon membranes were modified with poly(2-(methacryloyloxy)ethyl succinate) brushes to purify positively charged lysozyme from chicken egg white (Jain et al. 2010). Negatively charged sulfonyl matrices acting like ion exchangers were prepared on cellulose membranes to purify crude cationic urokinase (plasminogen-activating enzyme) from human urine at pH 4.5 (Hou and Zaniewski 1990). These affinity membranes can trap all positively charged enzymes or negatively charged enzymes at the same time. In other words, if one needs to have a particular type of enzymes, the concentrated enzymes from the membrane need further purification.

The second type of affinity membranes can provide more specific enzyme purification. These affinity membranes can bind enzymes through the interaction between a Lewis acid (electron pair donor), such as a chelated metal ion and an electron acceptor group, such as histidine or tryptophan residues on His-tagged recombinant proteins. This purification mechanism is the same as immobilized metal affinity chromatography (IMAC) which is a commercial protein purification method targeting His-tagged recombinant proteins. For example, poly(2-(methacryloyloxy)ethyl succinate) brushes of a porous nylon membrane were further functionalized with nitrilotriacetate (NTA)-Ni 2^{+} to bind His-tagged ubiquitin (Jain et al. 2010). These affinity membranes usually can rapidly get highly purified His-tagged proteins from cell extracts.

The third type of affinity membranes is using immobilized ligands to bind complementary enzymes. For example, heparin was covalently linked to a commercial membrane to bind antithrombin III which was recovered with 91 % purity and 97 % yield (Lutkemeyer et al. 1993).

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Affinity Separation and Crystallization of F_c Fragments

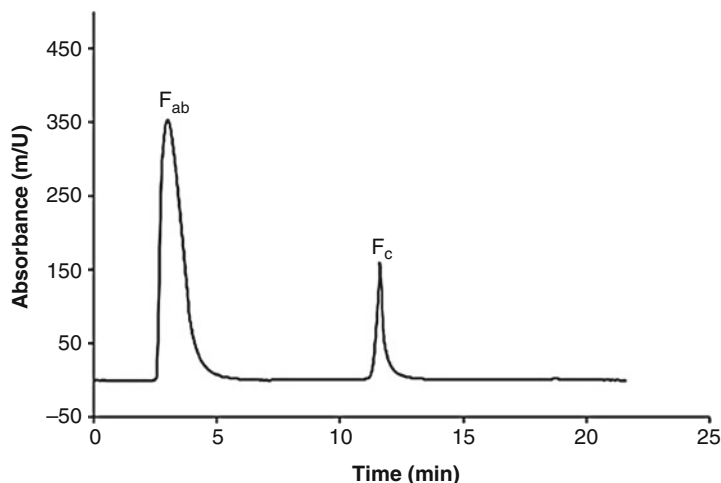
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Immunoglobulins are used by the immune system present in serum and tissue fluids to identify and neutralize foreign targets. Immunoglobulins are “Y”-shaped molecules comprised of two identical light chains (L) and two identical heavy chains (H) linked via disulfide covalent forces and via non-covalent interactions. Each chain has constant (C_L and C_H) and variable (V_L and V_H) domains (Holt et al. 2003). These form two antigen-binding fragments (F_{ab}) that specifically recognize and bind to antigen molecule and a constant fragment (F_c) which is responsible for

the effector function and biodistribution of the antibody (Beale 1987). Proteolytic digestion provides important information to determine an antibody molecule’s structure and function. Antibody molecules can be cleaved into fragments and each of these fragments has a distinct activity. A number of enzymes like papain, pepsin, ficin, bromelain, and elastase can be used for this purpose, papain being the most frequently used (Luo et al. 2002). Because of their smaller size as functional components of the whole molecule, antibody fragments offer several advantages over intact antibodies for use in certain immunochemical techniques and experimental applications. For this purpose, researchers have attempted to use smaller, more stable counterparts of antibodies and have also been searching for alternative ways to obtain antibody-like receptors (Haupt et al. 1998). Thus, bioengineered antibody fragments that are smaller than antibodies and have the ability to bind antigen bivalently have been promoted by the researchers (Cortese 1995). IgG molecule can be digested with papain for gaining F_{ab} and F_c fragments.

For the separation of F_{ab} and F_c fragments, HiTrap_r Protein A column can be used and collected the fragments by the fraction unit of the fast protein liquid chromatography (FPLC) system (Ertürk et al. 2011; Bereli et al. 2013; Aslıyüce et al. 2013). As shown in Fig. 1, a successful separation was observed and F_{ab} and F_c fragments

Affinity Separation and Crystallization of F_c Fragments, Fig. 1 FPLC chromatogram of IgG after digestion with papain (Ertürk et al. 2011)



Affinity Separation and Crystallization of F_c Fragments, Table 1 Chromatographic separation data

Fragment	t _R	N	K'	α	R _s
F _{ab}	3.06	52.39	1.19	6.14	-
F _c	11.16	1089.60	7.31	-	4.70

were separately collected. The retention times of the fragments were achieved at 3.06 and 11.64 min, respectively. The calculated chromatographic parameters such as t_R, N, k', α , and R_s values are summarized and given in Table 1. R_s value was calculated as 4.70 for F_c fragment. Because the R_s value should be higher than 1.0 for a good resolution of two peaks in such a chromatography system, the results for the resolution of F_{ab} fragment/F_c fragment can be accepted as good resolution values.

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Aged Carbon Membrane

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If the use of high-performance carbon membranes in gas separations is to be commercialized, the aging characteristics of such membranes will become important. Little work has been done on studying this aspect of carbon membranes, but some researchers have pointed out that there are significant problems related to the performance stability of carbon membranes (Jones and Koros 1995a; Lagorsse et al. 2004, 2005; Saufi and Ismail 2004). Although they are chemically and thermally resistant, carbon membranes generally suffer deterioration in performance upon exposure to substances that become strongly adsorbed, such as water vapor or oxygen. As carbon membranes have a sharp pore-size distribution with a critical size ranging from 0.3 to 0.7 nm, small changes in the effective size of the pore structures can markedly affect their permeability toward adsorbing gas molecules. In addition, constrictions in the pore system can occur as a result of chemisorption of oxygen or by strong adsorption of species having very low diffusivity because of their organophilic nature. Such species will block the pores in the membrane and attenuate the permeation of other species.

In a study of the effects of air oxidation and humidity at room temperature on the aging of carbon membranes, Menendez and Fuertes (2001) found the membrane stored in dry or humid air underwent a rapid loss of permeability, whereas membranes stored under propene or nitrogen were protected from damage. The researchers suggested that chemisorption of oxygen rather than physisorption of water is principally responsible for the loss of permeability that occurs when a fresh carbon membrane is exposed to air.

Jones and Koros (1994) found that carbon membranes are highly vulnerable to adverse effects of exposure to organic contaminants, even at concentrations as low as 0.1 ppm. Attempts to regenerate membranes after exposure to hydrocarbons by high-temperature (363 K) treatment in a vacuum were unsuccessful. Jones and Koros (1995a) also studied the effects of humidity on the O₂/N₂ selectivity and permeability of a carbon membrane by using feeds with relative humidities of 23–85 %. Some losses in performance occurred at all humidity levels, but this problem could be alleviated by rendering the surface of the membranes hydrophobic by coating them with thin layers of Teflon AF1600 or AF2400 (Jones and Koros 1995b). The resulting composite carbon membranes were significantly protected from the adverse effects of humidity.

Lagorsse et al. (2008) made a thorough investigation on the effects of exposure to air and humidity on the performance of commercialized carbon hollow fiber membranes, supplied by Carbon Membranes Ltd. (Israel). The production of these membranes involved pyrolysis followed by chemical vapor deposition and an activation step (Lagorsse et al. 2004). The researchers found that the membrane underwent a loss of permeability with time when exposed to pure oxygen or to air; however, the performance of the membrane ultimately stabilized after prolonged exposure. Attempts to regenerate the membranes by exposure to flowing nitrogen at 343 K or by treatment with propene and propyne as cleaning agents resulted in no significant recovery of permeability. However, no deterioration in permeability of these membranes was observed when they were stored under nitrogen. The researchers therefore concluded that aging of carbon membranes is caused exclusively by chemisorption of oxygen from air. On the other hand, humidity adversely affects the performance of membranes in multicomponent separation processes because water is strongly adsorbed, but diffuses relatively easily through the membranes. Heating under an atmosphere of hydrogen at 893 K to remove surface oxygen groups had some effect on stable surfaces protected from chemisorption of

oxygen. This treatment can be used to restore the permeation properties to those of fresh membranes.

These studies demonstrated that the effects of aging are more pronounced when membranes are stored under a high-humidity atmosphere and are exposed to air. The chemisorption of oxygen leads to the formation of C–O surface groups, thereby creating a more hydrophilic interface that favors increased adsorption of water. Adsorbed species can reduce the pore size of the carbon over time, leading to decreases in the permeability and selectivity of the membrane. Therefore, studies on the stability of carbon membranes will be an important aspect on research on such membranes in the future.

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Air Bubble Geometry

- [Honeycomb Membrane Structure](#)

Air Bubbling in Membrane Distillation

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Air bubbling is a common method that is used in membrane separation process to alleviate membrane fouling and improve flux. It also is a kind of membrane cleaning method. Till now, gas-liquid two phase flow has been well studied and widely used in microfiltration, ultrafiltration (Cabassud et al. 1997), membrane bioreactor (Psoch and Schiewer 2005), and other traditional membrane separation technologies.

Based on the above advantages of air bubbling, it has been introduced into membrane distillation (MD) process to alleviate membrane fouling and improve the heat and mass transfer efficiency. Researchers have introduced air bubbling into MD process and developed several new kinds of MD process.

The first application of air bubbling in MD process was firstly reported in 2008 (Ding et al. 2008) to concentrate the extract of traditional Chinese medicine (TCM). Air bubbling was used

in direct contact membrane distillation (DCMD) and the flow sheet is shown in Fig. 1.

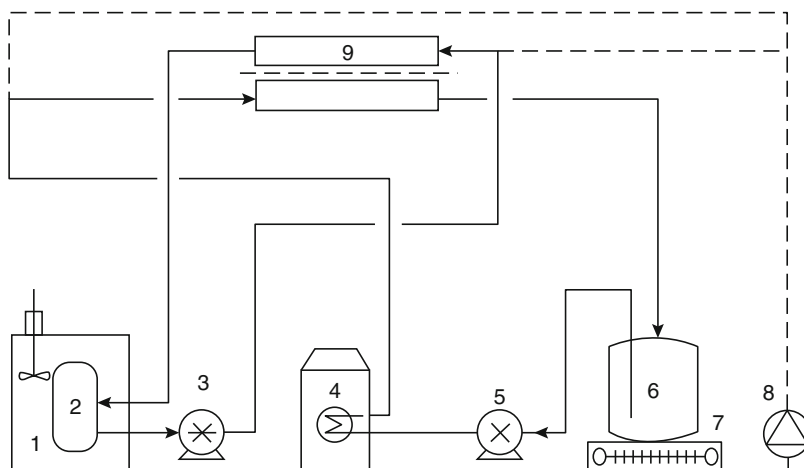
The TCM extract was heated to 43–62 °C and pumped to the module; another pump was used to circulate the permeate water (maintained at 25 °C) at the permeate side of the membrane module. The velocity of the feed and permeate flow in the membrane module ranged from 0.07 to 0.13 m/s. To mitigate membrane fouling, a fan was used to create gas bubbling at the feed side of the membrane module. This fan was also utilized to generate gas sparging at the permeate side for gas backwashing of the membrane. The concentration ratio (CR) was defined as the ratio of the volume of initial extract to the volume of concentrated extract to indicate the concentrating performance of the experiments.

The result showed that a sharp flux decline right after the air was introduced into the feed circulation, and the flux remained at much lower level when air was continuously injected. The explanation authors gave was that the bubbles occupied part of the liquid-contacting area in the membrane, thus reducing the effective membrane area, and when gas entered the membrane pores, this reduced the partial pressure of water vapor within the pores, thus reducing the driving force. To reduce these effects, intermittent gas sparging at the feed side at intervals of 20 min and lasting only 2 min was applied.

The effect of gas bubbling on the DCMD performance was shown in Fig. 2. It could be seen that flux declined rapidly in the beginning of the

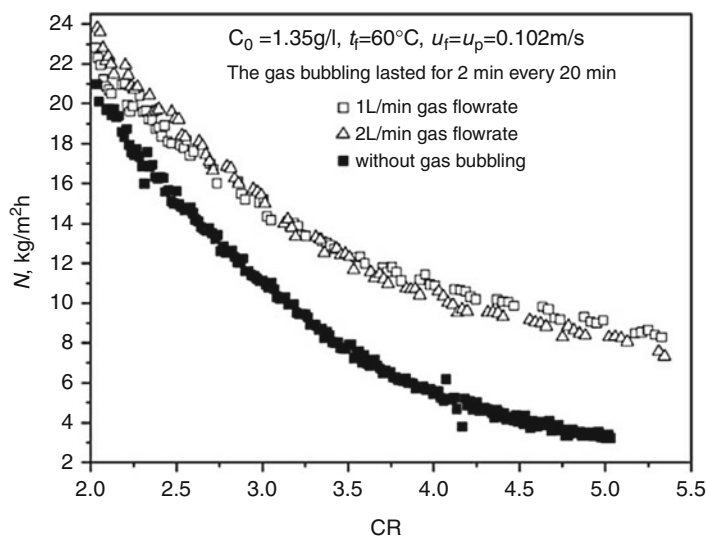
Air Bubbling in Membrane Distillation,

Fig. 1 Schematic of DCMD apparatus. (1) Thermostatic bath, (2) tank of TCM extract, (3) gear pump for extract circulation, (4) chiller, (5) gear pump for permeate, (6) permeate tank, (7) electric balance, (8) fan for gas bubbling, and (9) flat sheet membrane module



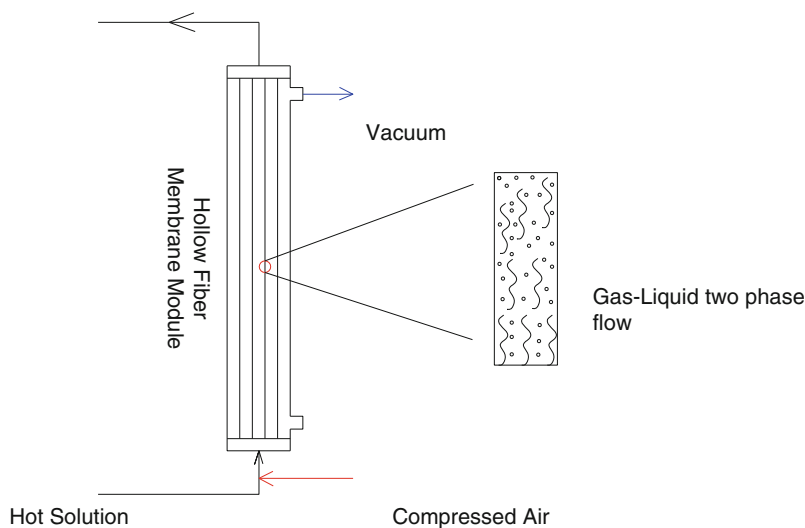
Air Bubbling in Membrane Distillation,

Fig. 2 Performance of DCMD using gas bubbling on the feed side



Air Bubbling in Membrane Distillation,

Fig. 3 Theoretic diagram of ABMD process



experiment and then slowly as a result of the very low-flux level at this time. The introduction of gas bubbling at the feed side resulted in a higher flux in the beginning of the experiment and a much slower flux decline. Very similar trends were observed with gas bubbling at 1 and 2 L/min which meant that increasing the gas flow rate did not result in further process enhancement.

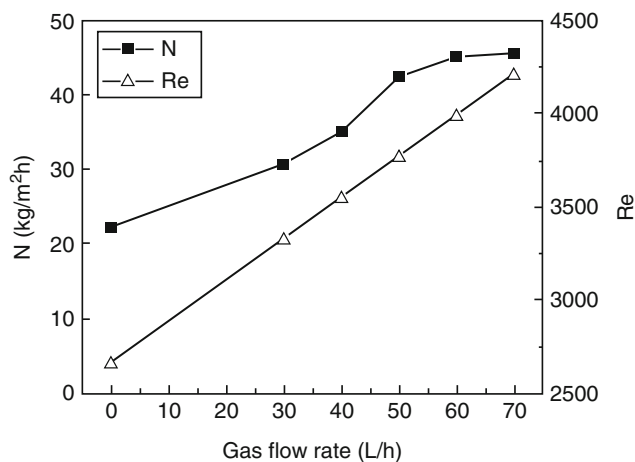
A novel air-bubbling vacuum membrane distillation (AVMD) process was constructed in 2011 (Wu et al. 2011) to investigate the enhancement effect of air bubbling on traditional VMD

process. Compressed air was pressed into the lumen side of the hollow fiber membranes together with the hot feed solution just at the inlet of membrane module to form gas-liquid two phase flow, as shown in Fig. 3.

The results showed that the permeate flux increased with the air flow rate and/or feed temperature increasing. For the VMD process, the permeate flux was $22 \text{ kg/(m}^2\text{h)}$ when tested at 75°C with a feed flow rate of 120 L/h and a vacuum pressure of 0.0085 MPa . While, the flux of AVMD process could reach $40 \text{ kg/(m}^2\text{h)}$

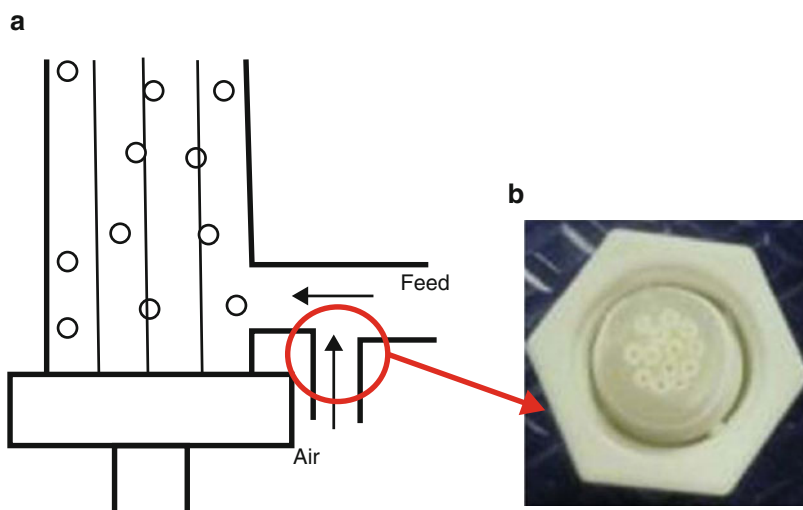
Air Bubbling in Membrane Distillation, Fig. 4

Effect of feed gas flow rate on the performance of AVMD process



Air Bubbling in Membrane Distillation, Fig. 5

(a) Air inlet connected to the membrane module; (b) Air nozzle



when gas was introduced into feed solution at the rate of 60 L/h, as shown in Fig. 4. For the two processes, flux both declined gradually as the feed concentration increased from 3.5 to 300 g/L, but it was much slower for AVMD process. SEM pictures showed that membranes used in AVMD process had lighter fouling than that in VMD process.

For elevated salt concentrations in the feed steam, gas bubbling was introduced into direct contact membrane distillation (DCMD) in 2013 (Chen et al. 2013) to examine its effect on the MD performance. In the paper, to characterize the performance improvement achieved by gas bubbling, the flux enhancement ratio Φ is defined:

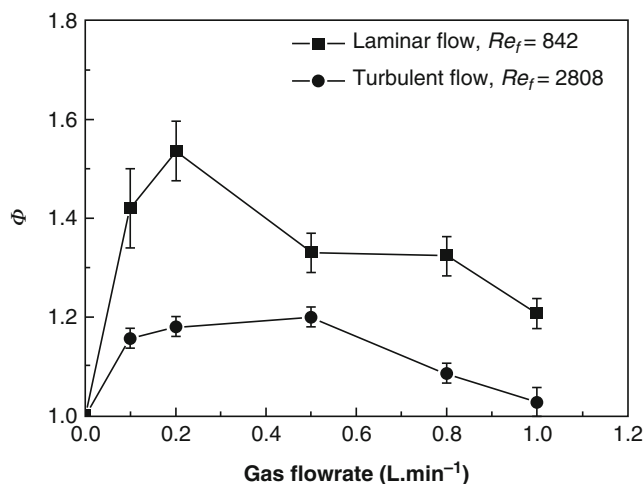
$$\Phi = \frac{J_{\text{gas}}}{J_{\text{nogas}}}$$

where J_{gas} and J_{nogas} are the permeate fluxes in the DCMD process with and without bubbling, respectively.

Gas bubbling is supplied by an air pump. The air inlet at the feed side entrance of the membrane module and the air nozzle for dispersing the air are shown in Fig. 5.

The results showed that the introduction of gas bubbling could effectively enhance MD flux, and the flux enhancement ratio could reach 1.72 at an optimized gas flow rate. When the condition was either a high feed operating temperature, low feed

Air Bubbling in Membrane Distillation, Fig. 6 Effect of gas flow rate on Φ in laminar and turbulent flows



and permeate Reynolds numbers, or a module with 45° inclined orientation, shorter fiber length, or lower packing density, a higher flux enhancement ratio could be achieved. Because air bubbling could enhance the turbulence of feed solution, temperature polarization was effectively reduced. However it was not that the bigger the gas flow rate, the higher the enhancement ratio. It was observed that beyond an optimal gas flow rate, the enhancement ratio fell, possibly due to excessive flow bypassing.

The effect of gas flow rate on Φ in laminar and turbulent flows was shown in Fig. 6. In the figure, it was observed that these two Φ curves had a similar trend. At first, Φ increased with increasing gas flow rate in the range of $0 \leq Q_g \leq 0.2 \text{ L min}^{-1}$ for the laminar flow and $0 \leq Q_g \leq 0.5 \text{ L min}^{-1}$ for the turbulent flow, while Φ decreased when gas rate was higher. Furthermore, the Φ value of the laminar condition was much higher than that of the turbulent flow when other conditions were the same.

In 2009, air bubbling was used in a hybrid process combining membrane distillation in a submerged membrane bioreactor (MDBR) to mitigate severe fouling and flux decline (Phattaranawik et al. 2009). The result showed that adding two inlets for air sparging at 2.5 L/min each near the potting at the center of the membrane bundle induced more turbulence at the membrane surface. Over 15 days, fluxes were

still relatively stable with an average value of $5.16 \text{ L/(m}^2\text{h)}$.

To sum up, air bubbling was an effective method in membrane distillation to enhance the performance of MD process. Due to the role of increasing turbulence of feed solution, air bubbling could promote the agitation and mix of feed solution to decrease the temperature and concentration polarization effect. In addition, the enhancing surface shear rate increases the remove of foulant from membrane surface at the feed side to inhibit the influence of membrane fouling.

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Air Dehydration by Membrane Technology

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Synonym

Membrane air dehydration

Air dehydration refers to removal of moisture from humid air and is also termed as air dehumidification and air drying. Due to the ubiquitous presence of moisture in air, air dehydration represents one of the largest membrane applications. Air dehydration through a membrane is essentially a vapor-phase separation process (Fig. 1), which can be carried out in two ways. In one way, moisture in the feed air diffuses across the membrane and is swept out of the membrane unit with a sweep gas stream (Fig. 1a). In another way, the permeated moisture is pulled away from the membrane unit by vacuum (Fig. 1b).

In the sweeping process, degree of air dehumidification will be limited by moisture content in the sweep gas and operation pressures, as explained by the following equations:

$$\Delta p = x_F \cdot p_F - x_S \cdot p_P > 0$$

$$x_F > \frac{x_P \cdot p_P}{p_F}$$

Low molar fraction of moisture in sweep gas (x_P), low permeate pressure (p_P), and high

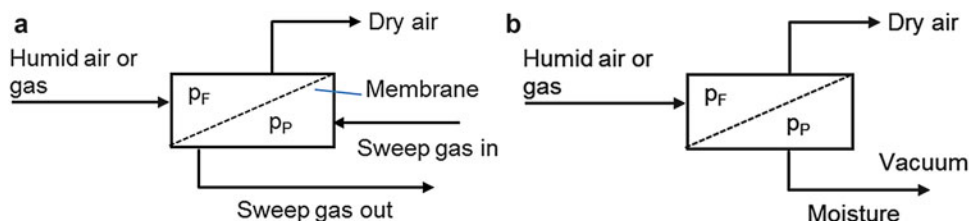
feed pressure (p_F) favor for deep dehumidification, i.e., allowing low moisture content in feed air (x_F).

If no sweep gas is used, the permeate pressure has to be decreased by vacuum to obtain a positive partial pressure gradient of water vapor across the membrane:

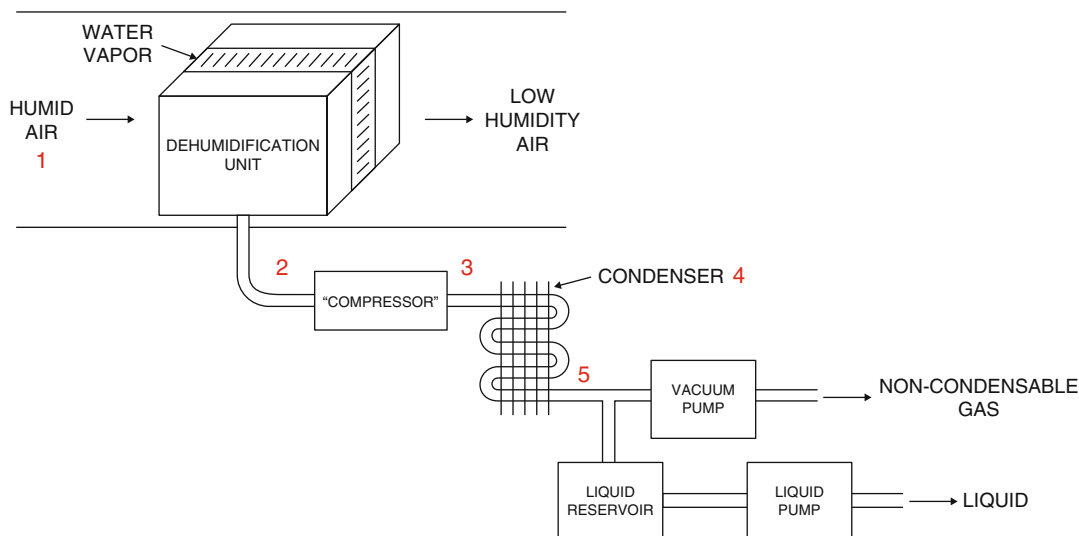
$$p_P < x_F \cdot p_F$$

Membrane dehydration is commonly used in industries for removal of moisture from pressurized air. In these applications, ambient air at atmospheric pressure is often used as sweep gas. Though moisture content (such as molar fraction) in the sweep air may be the same as in the process air, a significant partial pressure gradient of water vapor can be managed due to high pressures in the process air. For example, hollow fiber membranes are used for drying of the air pressurized to about 10 bar (Morgan et al. 1996). Air-sweep dehumidification can also be found in some laboratory membrane devices, such as Nafion membrane tubes for moisture exchange (Ye and LeVan 2003).

When humid air is at low or atmospheric pressures, using ambient air as a sweep stream is no longer practical, and pulling vacuum in the permeate side becomes necessary. In this case, several other pieces of equipment in addition to the membrane separator are required to make an integrated dehumidification system (Fig. 2). Such a membrane dehumidifier has been recently proposed and is still under development (Xing et al. 2013). An array of membrane units can be assembled together that the permeate sides of all the membrane units are connected to one common vacuum line. The vacuum is generated by the use



Air Dehydration by Membrane Technology, Fig. 1 Removal of moisture from humid air through a membrane



Air Dehydration by Membrane Technology, Fig. 2 Process flow diagram of a membrane dehumidification system

of a vacuum pump or gas compressor. The permeated moisture is compressed to a pressure above water dew point at environmental temperature so that water vapor is condensed into liquid-phase water by rejecting heat of condensation into environment. The condensed water is collected in a reservoir. Water in the reservoir may be discharged using a liquid pump, while residual air – noncondensable gas – is discharged into environment using a secondary vacuum pump.

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Air Enrichment, by Polymeric Magnetic Membranes

Anna Strzelewicz

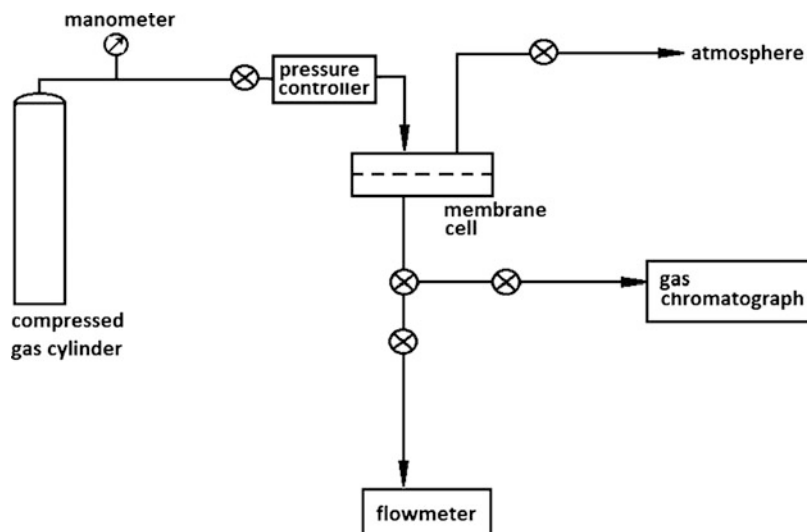
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The idea of using magnetic membranes for enrichment of air by oxygen is based on the observation that oxygen and nitrogen have quite different magnetic properties, i.e., oxygen is paramagnetic whereas nitrogen diamagnetic. The oxygen molecule is paramagnetic with a magnetic moment of $\mu_{O_2} = 2.73 \times 10^{-23} JT^{-1}$. Magnetic susceptibility of nitrogen is equal to $\chi = -150.8 \times 10^{-6} mol^{-1} = -2.5 \times 10^{-28} molecule^{-1}$ which corresponds only to $\mu = 2.5 \times 10^{-28} JT^{-1}$ in a magnetic field of 1 T, a value five orders of magnitude smaller than the O_2 magnetic moment (Morrish 1965; Borys et al. 2011).

Magnetic membranes are polymeric membranes (ethyl cellulose (EC) or poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)) with dispersed

Air Enrichment, by Polymeric Magnetic Membranes,

Fig. 1 Scheme of the experimental setup



magnetic powder (ferrite, praseodymium, and neodymium). The membranes are made by casting of appropriate polymer solution with dispersed magnetic powder in an external magnetic field of a specially designed coil (stable magnetic field with range of induction 0–40 mT). Removed from Petri dish membranes are dried in 40 °C for at least 2 days and then are stored in an exsiccator under the vacuum conditions ($p = 3$ mmHg). Collection of permeation quantities both for individual gases (O_2 , N_2) and for their mixture (air 21 % O_2 /79 % N_2) is measured in experimental setup (Fig. 1).

The measurements are carried out in room temperature for membranes with dispersed magnetic powder before and after magnetization in a field magnet with magnetic induction about 2.5 T. The setup furnished with a gas chromatograph allows to measure the oxygen and the nitrogen concentration in permeate. The main part of the experimental setup is diffusive chamber, where the membrane is put in the form of disk. The setup is used for a low-pressure (from 0.1 to 1.0 MPa) analysis of gas permeation. Transport coefficients can be calculated using flow rate data and percentage of air enrichment. The flow rate of the permeate can be recorded using a flowmeter.

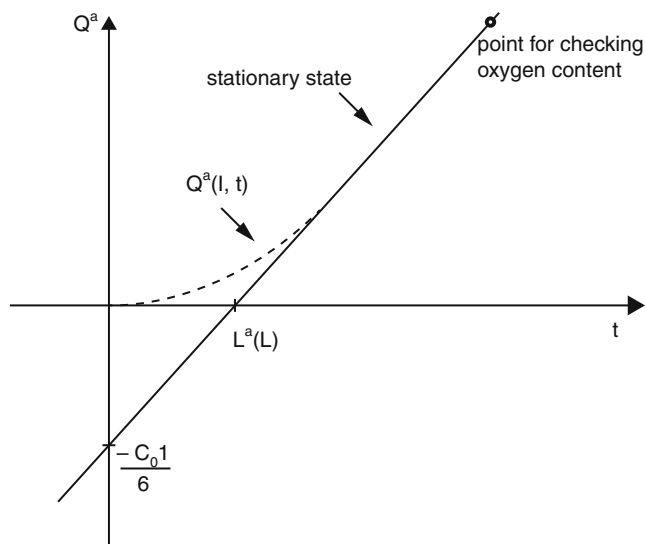
Integration of flux with respect to time allows to sketch a downstream permeation curve. Typical plot of $Q^a(l,t)$ versus time is presented in the Fig. 2.

Time-lag method and D1-D8 system allow to get some insight into the nature of the considered transport process. In papers (Strzelewicz and Grzywna 2007, 2008; Rybak et al. 2009a, b, 2012; Grzywna et al. 2010) a concept of magnetic membranes for air enrichment is explained. The authors observed an increase in the oxygen flux with respect to the nitrogen flux and the enrichment in the oxygen content of the permeate up to 55.6 % for ethyl cellulose magnetic membranes. Further permeation measurements done in polyphenylene oxide (PPO) magnetic membranes provided higher enrichments, up to 61.9 % (Table 1).

The transport of the molecules through the magnetic membranes can be modeled by a diffusion with a position-dependent diffusion coefficient. Such a diffusion coefficient reflects the changes in the membrane composition along the permeation axis. One can observe on the scanning electron microscope photograph (Borys et al. 2011) of the magnetic membrane cross section that the feed side of the membrane is

Air Enrichment, by Polymeric Magnetic Membranes,

Fig. 2 Downstream absorption permeation curve



Air Enrichment, by Polymeric Magnetic Membranes, Table 1 Air enrichment for various membranes (Strzelewicz and Grzywna 2007)

Membrane	B[mT]	Oxygen content in permeate [%]
EC + 1.38 g Nd	0.79	40.7 ± 1.1
EC + 1.49 g Nd	1.25	43.8 ± 1.1
PPO + 1.80 g Nd	1.70	54.1 ± 1.4
PPO + 1.80 g Nd	2.70	61.9 ± 1.5

composed of a pure polymer while the output side consists of the polymer with dispersed magnetic granules. When the magnetic field is too strong, then magnetic aggregates are created, which influence the permeation of gases. Detailed analysis of the available data and microscopy images allowed to arrive four conclusions (Borys et al. 2011):

1. There are magnetic channels formed around the magnetic granules.
2. The channels provide high permeability “highways” for the diffusion of permeating molecules.
3. The oxygen molecules, due to their paramagnetic properties, stick to these “highways” for a longer time than nitrogen, which is probably based on the interaction with the Weiss molecular field of the permanent magnet.
4. The magnetic field induces aggregation between oxygen and nitrogen which enhances

the transport of both nitrogen and oxygen by prolonging their residence in the channel.

The method of air enrichment by magnetic membranes seems to be effective and efficient.

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Air Gap Membrane Distillation (AGMD)

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AGMD is a configuration of membrane distillation (MD) in which an air layer is interposed between a porous hydrophobic membrane and the condensation surface (Fig. 1). In the process, volatile compounds (including water) present in a warm feed evaporate at the liquid/vapor interface formed at the membrane surface. The vapor is transferred through the membrane pores and the gas gap and finally condenses on a cold surface inside the membrane module. The driving force of the mass transfer in AGMD is the difference in vapor pressure on both sides of the membrane.

The air gap significantly reduces the heat loss by the membrane material, therefore the permeate flux could increase. On the other hand air gap forms a barrier for the vapor, and due to the mass transfer resistance the permeate flux decreases with an increase of the air gap width (Table 1) (Alkhudhiri et al. 2012). When the gap width is changed, the mechanism of heat transfer

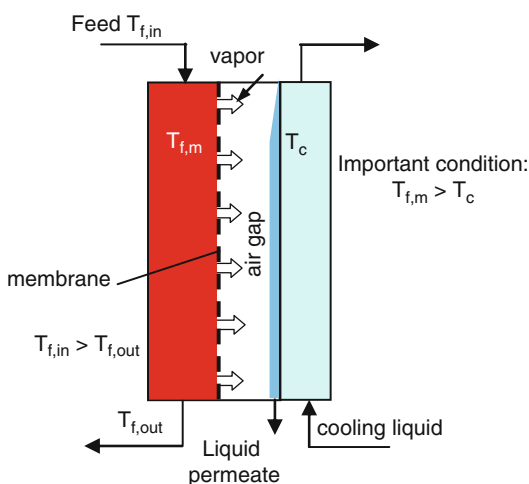
may be changed from pure conduction and diffusion to natural convection. The optimum of air gap width should be determined to achieve the best performance of the AGMD system taking into account a reduction of the heat loss and the value of the permeate flux.

Since in AGMD the permeate is condensed on the cold surface, the liquid permeate is separated from the membrane surface, which prevents the membrane wetting. Thus an important advantage of the process is the ability to remove the organic compounds from aqueous solutions.

The permeate flux in AGMD can vary from ca. 0.3 to 26 kg/m²h, depending on the operating conditions and feed composition. The rejection coefficient of nonvolatile species, e.g., NaCl, usually amounts close to 100 %. Generally, in AGMD the nonvolatile species present in a feed are almost completely retained, whereas volatile compounds are partially transferred through the membrane. The separation of compounds present in aqueous solutions using AGMD is based not only on the vapor/liquid equilibrium, but also the diffusion rate of the feed components through the gas filling the membrane pores and the air gap between the membrane and the condensation surface.

The air entrapped within the membrane pores and in the air gap can be considered as a stagnant film, thus the mass transfer in AGMD is generally described according to the ordinary molecular diffusion including both the air and noncondensable gases in the membrane pores and in the air gap. The air gap width is usually 10–100 times greater than the membrane thickness; therefore the membrane characteristics are usually neglected. In AGMD, the heat transfer includes the heat transfer through the feed boundary layer, through the membrane and the gas gap, condensation at the cold surface, and heat transfer through the condensate liquid boundary layer and to the cooling water. To optimize the AGMD systems, the effects of operating parameters should be taken into account (Khayet and Matsuura 2011).

The feed temperature strongly affects the permeate flux. Since the vapor pressure of aqueous solutions grows exponentially with temperature, the driving force increases for both water and volatile compounds present in a feed. Thus, the



Air Gap Membrane Distillation (AGMD),
Fig. 1 Schema of AGMD

Air Gap Membrane Distillation (AGMD), Table 1 Air gap effect on the permeate flux (reprinted from Alkhdhiri et al. (2012), copyright (2012) with permission from Elsevier)

Ref	Membrane material	Pore size (μm)	Feed	T_{in} ($^{\circ}\text{C}$)	Air gap (mm)	Permeate flux $\text{kg/m}^2\cdot\text{h}$
[5]	PVDF	0.45	Artificial seawater	60	1.9–9.9	$\approx 5\text{--}2.1$
[6]	PTFE	0.2	Isopropanol	50	1.62–0.55	$\approx 5.1\text{--}6.3$
[108]	PVDF	0.22	Sucrose	25.8	1–4	$\approx 1.7\text{--}0.8 \text{ l/m}^2\text{h}$
[18]	PTFE	0.2	NaCl (3.8 %)	60	0.3–9	$\approx 19\text{--}1.5$
[120]	PTFE	0.22	HNO_3 (4 M)	80	0.5–2	$\approx 5.3\text{--}4.25 \text{ l/m}^2\text{h}$
[123]	PTFE	0.45	HCl/water	60	4–7	$\approx 3.7\text{--}2.4$
[123]	PTFE	0.2	Propionic acid/water	60	4–7	$\approx 7.4\text{--}4.6$

Comments – the references can be found in the original paper

total permeate flux J_t (a sum of the water vapor flux J_w and the volatile compounds flux J_v) increases, but the selectivity of volatile solutes decreases with a feed temperature. The heat loss by conduction through the membrane material is lower at higher feed temperature which also explains the higher permeate flux.

An increase in the concentration of nonvolatile compounds in a feed reduces the J_t due to a decrease in the J_w . In the case of an increase of concentration of volatile compounds in a feed, the J_t and J_v increase, whereas the J_w decreases. It is associated with changes of the partial pressure of dissolved species and water. The selectivity of volatile compounds can be different depending on their properties and concentration in the feed and can be improved by an increase of their partial pressure by salt addition into a feed. Generally, a higher feed flow rate diminishes the effects of both temperature and concentration polarization and AGMD permeate flux increases. Different spacers can be applied to improve the hydrodynamic conditions. The effect of coolant temperature is not very significant because the heat transfer coefficient in the air gap dominates the overall heat transfer coefficient (Khayet and Matsuura 2011).

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Air Gap Membrane Distillation (AGMD), Applications of

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The separation using AGMD is based not only on vapor/liquid equilibrium but also on the diffusion rates of the feed components through the gas trapped in the membrane pores and the air gap between the membrane and the condensation surface. Nonvolatile compounds are rejected by a membrane in almost 100 %. Therefore, AGMD can be applied for desalination and production of high-purity water. A permeate with electrical conductivity as low as $4 \mu\text{S/cm}$ can be obtained from a solution with composition similar to seawater. Moreover, AGMD can be applied for the separation of volatile compounds. Since the vapor is condensed on the cold surface and the liquid permeate does not come into contact with a hydrophobic membrane, even the organic solutes can be separated without a risk of the membrane wetting. The air gap reduces considerably the heat loss and the temperature polarization which improve the separation efficiency of AGMD; however, this leads simultaneously to a significant decrease in the permeate flux. The decrease depends strongly on the width of the air gap. The air gap is about 10–100 times thicker than the membrane, so the

Air Gap Membrane Distillation (AGMD), Applications of, Table 1 Application of air gap membrane distillation

Area	Membrane material	Application
Desalination	PTFE, PVDF Modified ZrO ₂ , modified Al ₂ O ₃ , modified TiO ₂ , modified aluminosilicate	Water and wastewater treatment, production of pure water, solar-powered desalination, geothermal wastewater treatment
Food industry	PVDF, PTFE	Fruit and vegetable juice concentration, milk concentration, sugar and gelatine solution concentration, ethanol concentration
Biotechnology	PTFE, PVDF	Ethanol separation from a broth
Others	PTFE, PVDF	Methanol, isopropanol concentration, separation of azeotropic mixtures HCl/water, propionic acid/water, formic acid/water, separation of radioisotopes ¹⁸ O and ¹⁸ F, concentration of wastewater containing isotopes, HI and H ₂ SO ₄ concentration Separation/removal of HNO ₃ , HCl, formic acid, acetic acid, propanone from aqueous solutions

PTFE polytetrafluoroethylene, *PVDF* polyvinylidene fluoride

effect of air inside the membrane can be neglected. AGMD creates the opportunity for the separation of species forming the azeotropic solutions. It is attributed to the difference in the diffusion coefficients of volatile compounds present in a feed through the gas gap (Khayet and Matsuura 2011). Thus, AGMD can find the application in water and wastewater treatment, biotechnology, food industry, etc. (Table 1).

The plate and frame, tubular, capillary, and very frequently spiral wound modules equipped with porous hydrophobic membranes are used in AGMD.

The main area of AGMD application is desalination. The desalination pilot plants combining AGMD with solar energy collectors were developed, especially for operation in arid and semiarid remote regions with a lack of electricity and drinkable water but with high solar radiation (Table 2). The production of potable water, e.g., from plants installed in Jordan was of 100 L/day (utilizing brackish water) and 1 m³/day (Fig. 1) (utilizing untreated seawater from the Red Sea). The installations were equipped with AGMD spiral wound modules with area of 10–40 m², respectively. Long-term experiments have demonstrated that the average salt rejection was 98 % (Qtaishat and Banat 2012; Khayet and Matsuura 2011). Distillate conductivity of 3–5 µS/cm can be obtained for brackish water feeding. Despite the advantages such as the ability to desalinate high saline

feedwater, fitness for intermittent energy supply, and the ability to use direct solar heat without heat storage, the plants have not been commercialized or implemented in a large scale. This is mainly because reverse osmosis (RO) is considered as more economical and energy-efficient desalination process (Saffarini et al. 2012). However, the AGMD/solar energy systems are still in progress and find a growing interest.

Another field of AGMD application is food processing. Figure 2 presents the possibility of juice concentration by AGMD to achieve much higher feed concentration than using RO. Low processing temperature allows to concentrate the solutions sensitive to high temperature and provides a good quality of juice concentrate (Kimura and Nakao 1987). The concentration of milk demonstrated that the membranes were easily fouled by milk fat and the permeate flux decreased very fast (Khayet and Matsuura 2011).

Ethanol preferentially vaporizes from the aqueous feed and is concentrated in the permeate. Since in AGMD the liquid ethanol does not come into contact with a membrane, it can be separated from a fermentation broth and concentrated without a risk of the membrane wetting. It was found that a salt addition into diluted ethanol increases alcohol selectivity (Khayet and Matsuura 2011).

AGMD can be useful in breaking the azeotropic mixtures of water and hydrochloric or propionic acids. This phenomenon was associated

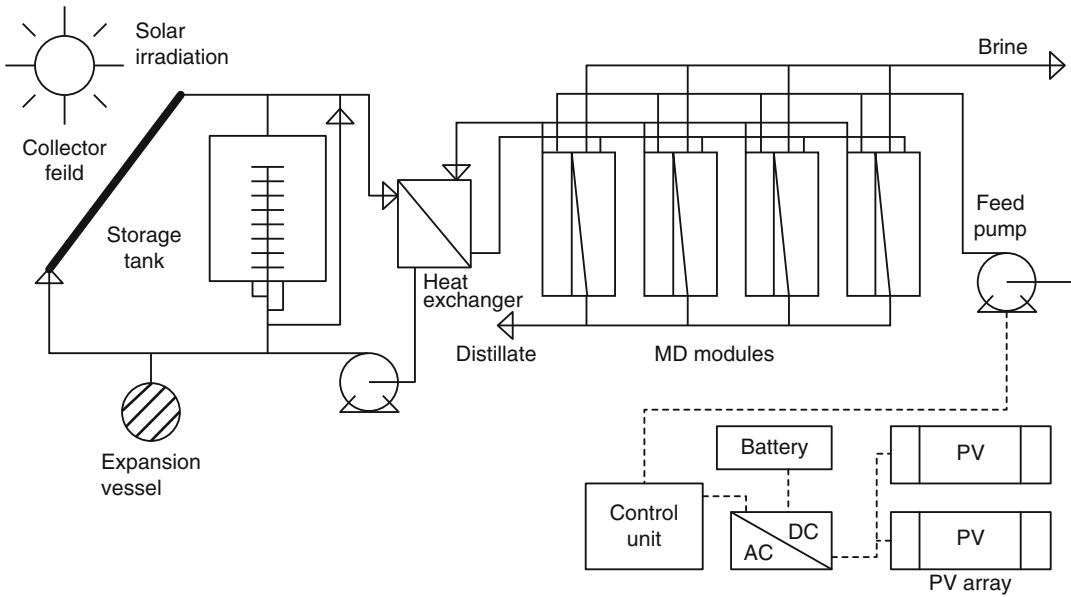
Air Gap Membrane Distillation (AGMD), Applications of, Table 2 Timeline of solar-powered membrane distillation systems and their general features (Adapted from Saffarini et al. 2012)

Year	Location	MD type	Membrane type/material	Feedwater type	Energy system type		Solar collector type
					Thermal	Electrical	
1991	New South Wales, Australia	DCMD	Hollow fiber/ N/A	N/A	Solar collector	Grid	N/A
1995	New South Wales, Australia	AGMD	Spiral wound/ PTFE	N/A	Solar collector	Grid	VPC
1997	Tokyo, Japan	N/A	N/A/N/A	N/A	Solar collector	PV	N/A
1999	Texas, USA	AGMD	N/A/N/A	N/A	Solar pond	Grid	N/A
1999	Irbid, Jordan	DCMD	N/A/PTFE	Brackish	Solar still	Grid	N/A
2003	Freiburg, Germany	AGMD	Spiral wound/ PTFE	Freshwater	Solar collector	Grid	FPC
2004	Texas, USA	AGMD	N/A/N/A	NaCl solution	Solar pond	Grid	N/A
2007	Irbid, Jordan	AGMD	Spiral wound/ PTFE	Brackish	Solar collector	PV	FPC
2007	Aqaba, Jordan	AGMD	Spiral wound/ PTFE	Seawater	Solar collector	PV	FPC
2008	Alexandria, Egypt	AGMD	Spiral wound/ PTFE	Brackish	Solar collector	PV	FPC
2008	Mexico	DCMD	Hollow fiber/ N/A	N/A	Solar collector	Grid	FPC
2009	Almeria, Spain	AGMD	Flat sheet/ PTFE	Seawater	Solar collector	Grid	CPC
2009	Hangzhou, China	VDM	Hollow fiber/ PP	Brackish	Solar collector	Grid	N/A
2009	Nevada, Reno, USA	Vacuum enhanced DCMD	N/A/N/A	N/A	Solar pond	N/A	N/A
2009	Gran Canaria, Spain	AGMD	Spiral wound/ PTFE	Seawater	Solar collector	PV	Double glass FPC
2011	Marina Barrage, Singapore	VMEMD	Flat sheet/ PTFE	Seawater	Solar collector	PV	N/A

DCMD direct contact membrane distillation, VMD vacuum membrane distillation, PP polypropylene, N/A not available, PV photovoltaic panels, VPC vacuum plate collector, FPC flat plate collector, CPC concentrated parabolic collectors, VMEMD vacuum multi-effect membrane distillation

with the differences in the acid-air and water-air diffusion rates in the air gap. In AGMD the hydrochloric acid/water azeotrope was shifted to higher acid concentration, and the azeotrope was eliminated in the propionic acid/water system. It was found that the heavy gases such as SF₆ help more in eliminating the azeotropic point than the lighter ones as air or He (Khayet and Matsuura 2011).

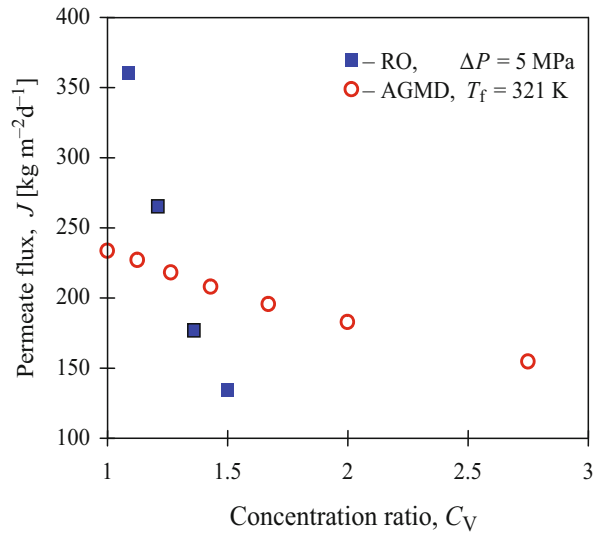
AGMD was successfully used for the concentration of a mixture of HI and H₂SO₄, compounds of great interest for H₂ generation in thermochemical water-splitting cycle (Khayet and Matsuura 2011). AGMD has also a great potential in the application in the environment protection area. Therefore, this technique requires more studies, devoted especially to a long-term performance and membrane life.



Air Gap Membrane Distillation (AGMD), Applications of, Fig. 1 Schema of the large system (two-loop desalination system) of desalination using AGMD solar

powdered (Reprinted from Qtaishat and Banat (2012), copyright (2012) with permission from Elsevier)

Air Gap Membrane Distillation (AGMD), Applications of, Fig. 2 The comparison of the permeate flux during concentration of the mandarin orange juice using RO and AGMD (Adapted from Kimura and Nakao 1987)



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Air Products

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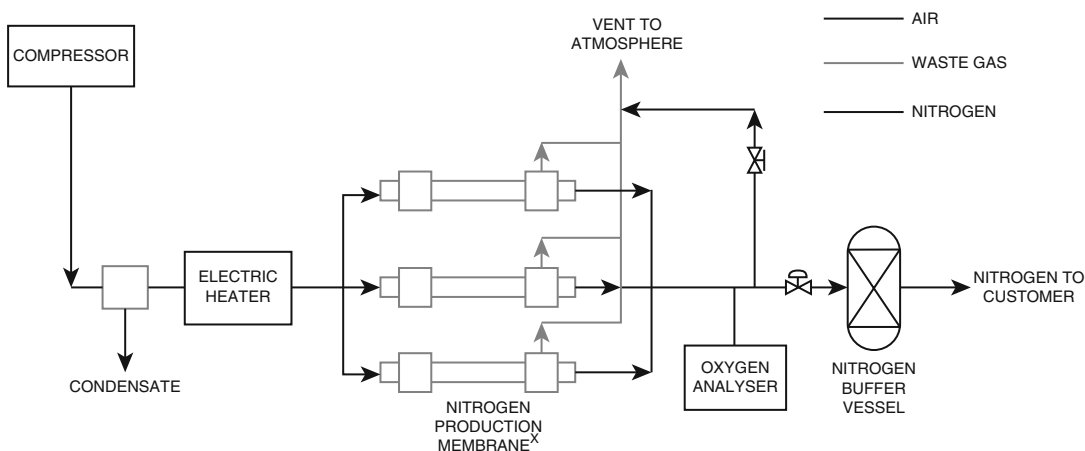
The majority of air separation is done by cryogenic distillation; however, for several small applications a gas separation membrane is desirable. The key commercial gaseous products made from air by membranes are nitrogen, oxygen enriched air, and dry air. Further, gas separation membranes in hybrid system with a cryogenic process is used to produce Argon (Agrawal and Xu 1996) and with an adsorption process to produce high concentration oxygen enriched air (Choe et al. 1997).

In membrane nitrogen production systems (Drioli and Barbieri 2011), the compressed air is fed on one side of the membrane; oxygen, argon, carbon dioxide, and water which have higher permeation than nitrogen, permeate through the membrane leaving nitrogen behind. A schematic of the membrane nitrogen generation system is shown in Fig. 1.

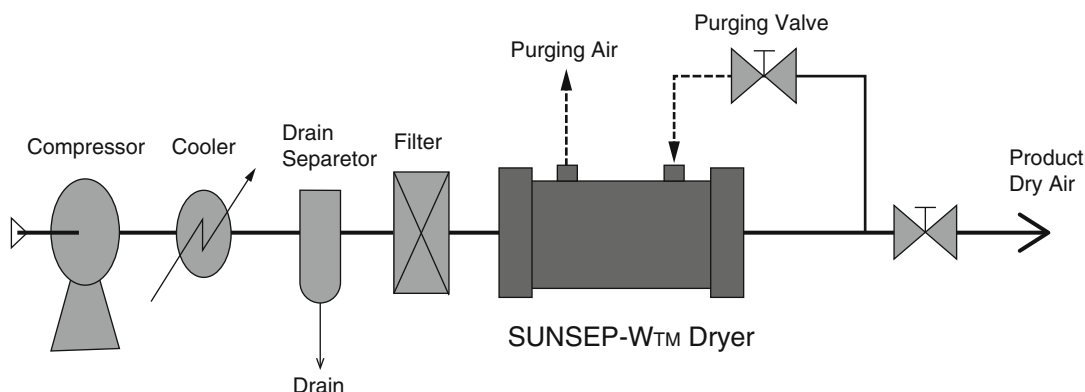
The compressed air at a temperature of 80–100 °C and a pressure of about 1000 kPa (135–150 psi) is purified by the use of coalescing filter and fed to the membrane module. The productivity and purity of the nitrogen produced is controlled by the use of a product pressure valve. Membrane systems produce nitrogen at a concentration ranging from 95 % to 99.9 %. However, due to the modest selectivity (<8) of air separation membranes, production of high purity nitrogen is not economically favorable. Key producers of nitrogen separation membranes are Air Products, Air Liquide, and Ube. Other nitrogen membrane producers are: Generon Systems, Aquillo and Parker Heniffin.

Dry air with dew point up to -40 °C (-40 °F) is produced by removing moisture from the atmospheric air using a water permeable membrane which are either made of glassy polymers (polysulfone, polyimide, etc.) or fluorine containing ionomers. Schematic of a typical air drying system is shown in Fig. 2.

In air drying system, clean wet air is fed under pressure on one side of the membrane module and dry air at slightly reduced pressure is recovered as retentate. In some systems, an internal or external



Air Products, Fig. 1 Schematic of nitrogen generation system (Reproduced with permission from Air Products)



Air Products, Fig. 2 Typical air drying system (Courtesy: AGC Chemicals Americas)

dry air sweep is used to prevent water buildup on the membrane in permeate, which retards membrane performance (Morgan et al. 1996).

In some instances, membrane systems are used to produce oxygen enriched air with oxygen concentration $<30\%$ O_2 . Mostly, rubbery membranes of modest selectivity (2–3) and high oxygen flux are used for this application³. The membrane system used is similar to that used for nitrogen production described above. Sometimes, use of vacuum on the permeate side is preferred over the use of a compressor for the production of oxygen enriched air.

Air Separation

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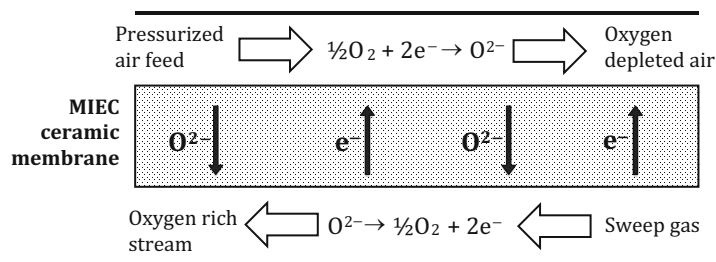
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Air separation technology is used for the production of oxygen, nitrogen, and rare gases that are present in air such as argon and neon. There are two fundamental approaches to air separation, which are cryogenic and non-cryogenic processes. The cryogenic process which is carried out in distillation column has the capability to deliver large and high purities of products, while the non-cryogenic which is based on absorption and membrane technologies is more suitable for on-site production, which is most common for small and medium throughputs.

Air Separation,
Fig. 1 Schematic representation of the oxygen transport in MIEC ceramic membrane



Membrane technology for air separation has developed rapidly in recent years. Polymeric and ceramic membranes have been used commercially for oxygen production. Polymeric membranes operate based on the difference in rates of diffusion of oxygen and nitrogen through a membrane. Due to the smaller size of the oxygen molecule, most membrane materials are more permeable to oxygen than to nitrogen. Materials such as polysulfone or acetate membranes make it possible to permeable oxygen five times than of nitrogen. Membrane units capable of producing nearly 600 tonnes per day nitrogen have been built (Castle 2002). A major benefit of polymeric membrane separation is the simple, continuous nature of the process and operation at near ambient conditions (Smith and Klosek 2001); however, the low separation factor of two to six limits the polymeric membrane to produce oxygen-enriched air rather than pure oxygen (Zhu et al. 2008).

Production of pure oxygen from air can be achieved by using ceramic membrane system at elevated temperatures, typically in the range of 800–900 °C (Hashim et al. 2011). The oxygen transporting through this type of membrane is in the form of oxygen ions instead of oxygen molecules; therefore, the pure oxygen is obtained. Enormous efforts have been directed to ceramic membranes with mixed ionic–electronic conducting (MIEC) characteristics. Among them, perovskite-type (ABO_3) ceramic membranes exhibit the highest oxygen permeability due to their high ionic and electronic conductivity. The perovskite oxide based on $\text{La}_{1-x}\text{A}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ achieved very high oxygen permeation fluxes as reported by Teraoka et al. (1985).

Interestingly, the oxygen separation from air in MIEC ceramic membrane system requires neither electrodes nor an external circuit to operate. As depicted in Fig. 1, the electronic conductivity itself performs as an internal short circuit that involves oxygen partial pressure gradient. The oxygen molecule permeates from the high oxygen partial pressure side to the low oxygen partial pressure side, while the overall charge neutrality is maintained by counterbalancing the flux of electrons (Liu and Gavalas 2005). Several industrial gas companies are working on developing ceramic membranes for oxygen separation from air at high temperatures. Air Products and Chemicals has developed an ion transport membrane (ITM) system, which is based on patented, high-temperature ceramic membranes for the production of oxygen from air separation (Hashim et al. 2011). Praxair is also working on oxygen-conducting ceramic membrane systems that are specially designed to separate oxygen from air at elevated temperature environment (Hashim et al. 2011).

Cross-References

► Oxygen Separation

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Al₂O₃ Porous Membranes

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Synonyms

[Aluminum \(III\) oxide porous membranes or alumina porous membranes](#)

Characteristics

Al₂O₃ is an amphoteric oxide that exhibits polymorphic crystalline forms upon temperature treatment. A wide variety of alumina powders are commercially available with different particle sizes.

Alumina porous membranes are commercially available inorganic ceramic membranes widely used in membrane processes related to water treatment essentially. They are shaped in monolith, honey comb, flat, monochannel, and multichannel configurations or as thin films.

Alumina membranes may be prepared by anodic oxidation of aluminum foil to design well-ordered and straight pore channels in the membrane or by sol-gel route using colloids or Al molecular precursors to yield porous supported membranes. In addition, alumina macroporous supports are also used for multilayered structures of other oxide or non-oxide materials. More recently, alumina porous membranes found a new application as hard template for the fabrication of nanotubes and nanowires through

electrodeposition and alumina membrane etching (Burggraaf and Cot 1996; Lee and Pope 1994).

The filtration process and therefore the elimination of different species from polluted water, for example, strongly depend on the type of membrane used, its porosity, and pore size. As recommended by IUPAC, porous membranes are classified according to their connected pore size being microporous for pore diameters lower than 2 nm, mesoporous for pore diameters in the range 2–50 nm, and macroporous for pore sizes superior than 50 nm (Koros et al. 1996). Respectively, porous membranes will be applied to separation processes such as nanofiltration, ultrafiltration, and microfiltration.

The synthesis of macroporous and mesoporous membranes is often made by consolidation of particles followed by thermal removal of organic additives. Going to nanofiltration application, the microporous network is directly prepared from a sol containing particles lower than 10 nm followed by an appropriate sintering step.

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Alamine 336

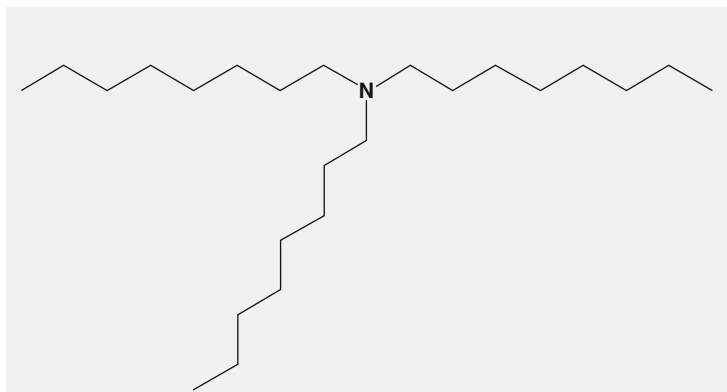
Karel Friess

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Synonyms

[Alamine 336S](#); [Alamine 336S](#); [Farmin 08](#); [Octanamine](#); [Tricaprylamine](#); [Tridioctylamine](#); [Tri-*n*-octylamine](#); [Tri-*n*-caprylamine](#); [Trioctylamine](#)

Alamine 336,
Fig. 1 Schematic structure
 of Alamine 336



The IUPAC systematic name is *N,N*-dioctyl-1-octanamine (Fig. 1). Alamine 336 is colorless ($C_{24}H_{51}N$, CAS Reg. No. 1116-76-3) or light yellow liquid (mixture of Tri C8-10 Alkyl Amines, $C_{27}H_{57}N$ – CAS Reg. No. 57176-40-6, produced by Cognis Corp., now part of BASF). If released to air, estimated vapor pressure is about 0.007 Pa at 25 °C. It is moderately toxic by ingestion and intraperitoneal routes; when heated to decomposition, it emits toxic vapors of NO_x (Zhu et al. 2012). Manufacturing of Alamine 336 is possible by catalytic amination of octanol (Li et al. 2011) or by catalytic hydrogenation of caprylonitrile (Lazier 1940). It is used as the extractant for reactor fuel processing (Moyer and McDowell 1981), for dye identification (Puttemans et al. 1982), and for metal adsorption (Tasker et al. 2003) and recovery from diluted aqueous solutions (Kislik 2012; Coca et al. 1990; Sun and Lee 2011). Mixtures of Alamine 336 with meta-xylene can be successfully applied for extraction metal ions from their strong acidic aqueous chloride solutions (Sayar et al. 2007). Alamine 336 can be also used for specific extractions in biotechnology, e.g., separation of carboxylic acids (Tamada et al. 1990; Yordanov and Boyadzhiev 2004), and in supported liquid membranes (San Román et al. 2010; Dzygiel and Wieczorek 2010) (Table 1).

Alamine 336, Table 1 Properties of Alamine 336 (Steele et al. 1996)

Molar mass	353.67	$g \cdot mol^{-1}$
Melting point	−34.6	°C
Boiling point	363.5	°C
Density	0.818	$g \cdot cm^{-3}$ at 25 °C
Viscosity	$7.86 \cdot 10^{-2}$	Pa·s at −34.6 °C
Surface tension	$3.48 \cdot 10^{-2}$	$N \cdot m^{-1}$ at −34.6 °C
Constant pressure heat capacity of liquid	750.8	$J \cdot mol^{-1} \cdot K^{-1}$ at 25 °C
Solubility in chloroform	0.1	$g \cdot cm^{-3}$ at 25 °C
Solubility in water	0.050	$mg \cdot dm^{-3}$ at 25 °C

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Alamine 336S

► Alamine 336

Alamine 336S

► Alamine 336

Albumin Purification with Affinity Membranes

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Nearly 175 years ago, a very accurate description of the properties of human serum albumin (HSA) was available (Ancell 1839). HSA is one of the most abundant proteins in plasma and, together with immunoglobulin, constitutes 80 % of all plasma proteins. In addition to plasma, HSA is also found in tissues and bodily secretions throughout the body. It has several physiological functions in vivo, which contribute significantly to colloid osmotic blood pressure and aid in the transport, distribution, and metabolism of many endogenous and exogenous substances (He and Carter 1992). The ethyl alcohol fractionation is the oldest process of industrial fractionation of blood proteins but it cannot produce sufficiently pure albumin (Stotz et al. 1990). Of all purification methods, chromatography may be the best candidate for minimizing process-generated albumin heterogeneity. Affinity chromatography is a well-established method for the purification of proteins, and it is based on highly specific molecular recognition. Conventional packed-bed column chromatography is often limited by long processing times due to low flow-rates, which result from the high pressure drop (Denizli et al. 1999). In order to overcome these operational limitations, microporous membrane adsorbers have been developed (Ghosh 2002). Microporous membranes as a support for chromatography have several potential advantages. A configuration in which the feed solution flows

Albumin Purification with Affinity Membranes, Table 1 Albumin adsorption capacities for various membrane affinity adsorbents

Adsorbent	Ligand	Ligand loading	Q _{max}	References
Polyethylene hollow fiber	CB F3GA	52 µmol/mL	6.5 mg/mL	(Wolman et al. 2000)
PTFE membrane	CB F3GA	89.8 µmol/g	85.3 mg/g	(Gu et al. 2007)
P(GMA-DMAA) hollow fiber	CB F3GA	117 µmol/g	15.3 mg/mL	(Wolman et al. 2005)
Polyamide hollow fiber	R. Green HE4BD	39.4 µmol/g	86.7 mg/g	(Yavuz and Denizli 2004)
PTFE membrane	CB F3GA/Zn ²⁺	not reported	198.5 mg/g	(Gu et al. 2007)
Polyamide hollow fiber	Cu ²⁺	150 µmol/g	226.0 mg/g	(Uzun and Denizli 2002)
	Ni ²⁺	250 µmol/g	289.0 mg/g	(Uzun and Denizli 2002)
	Co ²⁺	250 µmol/g	195.0 mg/g	(Uzun and Denizli 2002)

through the membrane provides a very short, wide bed; thus, high velocities and very short residence times are attainable with modest transmembrane pressure drops. Elimination of diffusional resistance usually leaves a system controlled by much faster binding kinetics, thereby enabling adsorptive separation of proteins, typically, one-tenth the time common for packed columns. Adsorptive membranes exhibit high binding capacities similar in magnitude to packed columns and using stepwise elution, proteins can rapidly be concentrated tenfold or more with 85–100 % recovery. Analytical separations equivalent to those of column chromatography are reached by using sufficient numbers of membrane stacks and gradient elution methods. The linear scalability of the membrane systems further adds to the attractiveness of the technology. When dealing with viscous mediums such as blood, mass transfer in a diffusive-transport mode is more efficient, where the liquid is made to flow tangentially past the membrane surface while the adsorbate diffuses into the microporous membrane to meet the selective ligand immobilized there. Several ligands can be used for the affinity separation of albumin as summarized in Table 1.

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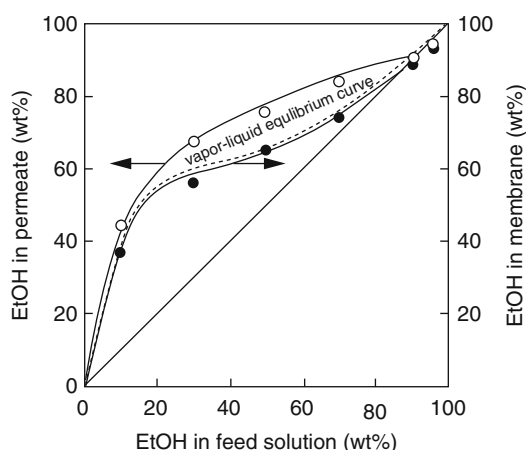
Alcohol and Water Separation

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Cross-linked poly(vinyl alcohol) (PVA) composite membranes have been used in commercial PV plants for dehydration of ethanol beyond the

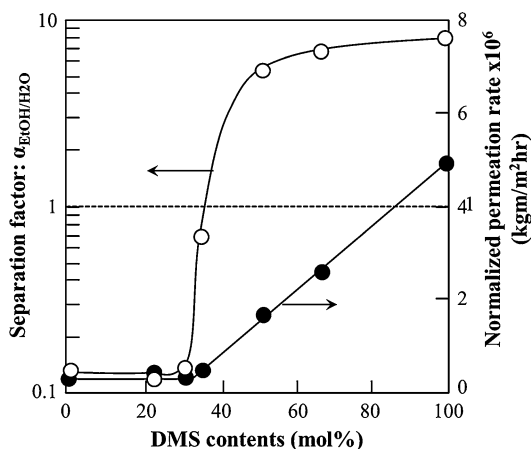
azeotrope. However aqueous ethanol solutions that can be produced by bio-fermentation are dilute (about 10 wt.%). Therefore, if ethanol/water-selective membranes with high efficiency can be prepared, the distillation process in the first stage to obtain an azeotrope can be replaced ethanol-/water-selective membrane which is very advantageous for reduction of energy cost. There are fewer reports on ethanol-/water-selective membranes compared with those of water/ethanol-selective membranes. One reason why the development of efficient high-performance ethanol-/water-selective membranes is difficult can be attributed to the fact that ethanol has a larger molecular size than water and must be preferentially permeated through the membrane. In fact, permeation and separation in a pervaporation (PV) process through dense membranes are based on the solution-diffusion mechanism (Binding et al. 1961; Aptel et al. 1974). Therefore, when it is required that ethanol molecules with larger molecular size preferentially permeate from an aqueous ethanol solution, it cannot be expected to be separated by the diffusion process. Consequently, only a difference of solubility selectivity in the solution process in which both ethanol and water components are dissolved can contribute to the separation. Figure 1 shows the ethanol concentration in the



Alcohol and Water Separation, Fig. 1 Permeation and separation characteristics of aqueous ethanol solutions through a PDMS membrane during PV

permeate through a poly(dimethylsiloxane) (PDMS) membrane during PV and that sorbed into a PDMS membrane. These results support the hypothesis that the difference in the solubility of the permeants contributes to the ethanol/water selectivity. PDMS membranes show high ethanol/water selectivity, but their mechanical strength is weak, and it is difficult to prepare thin membranes from PDMS. In order to obtain both ethanol/water selectivity and mechanical strength, graft copolymers composed of PDMS macromonomer and vinyl monomers were synthesized.

Graft copolymer membranes, which were either ethanol or water selective, were prepared by copolymerization of a dimethylsiloxane (DMS) macromonomer with methyl methacrylate (MMA) (Miyata et al. 1995, 1996). Two glass transition temperatures (T_g) were observed at about 120 °C and -127 °C in the graft copolymer membranes. Transmission electron micrograph (TEM) demonstrated that the PMMA-g-PDMS membranes showed microphase-separated structures. When an aqueous solution of 10 wt.% ethanol was permeated through the PMMA-g-PDMS membranes by PV, the ethanol concentration in the permeate and the permeation rate increased drastically with the DMS content in the copolymer. In particular, at a DMS content of less than



Alcohol and Water Separation, Fig. 2 Effects of the DMS content on the normalized permeation rate (O) and separation factor (●) through the PMMA-g-PDMS membrane during PV. Feed: aqueous solution of 10 wt.% ethanol. Dashed line is the feed composition

Alcohol and Water Separation, Table 1 Performance of ethanol-/water-selective membranes

Membrane	Feed (wt %)	Method	Applied temperature (°C)	$\alpha_{\text{EtOH/H}_2\text{O}}$	NPR ^a (kg $\mu\text{m}^2\text{h}^{-1}$)	References
PDMS	7	PV	25	11.8	2.1	Eustache and Histi (1981)
PTMSP	7	PV	25	11.2	1.1	Ishihara et al. (1986)
PTMSP	10	PV	30	12	4.5	Masuda et al. (1986)
PEA-g-PDMS/PTMSP ^b	10	PV	40	20	24.1	Uragami et al. (2000); Uragami and Shinomiya (1991)
PPP-g-PDMS	7.28	PV	30	22.5	5.5	Nagase et al. (1989)
PSt-g-PhdFDA (7.6/12.4)	8	PV	30	45.9	0.6	Ishihara and Matsui (1987)
TFE/ <i>i</i> -OcVE/C ₁₈ VE terpolymer (50/25/25)	15	PV	50	7.13	5	Kashiwagi et al. (1988)
Modified silicone	10	PV	40	3.65	11	Uragami and Shinomiya (1991)
Modified silicone	10	TDEV	−30/40	19.3	16.6	Miyata et al. (1996)
PDMS	10	PV	40	7.44	6.4	Miyata et al. (1995, 1996)
PDMS	10	TDEV	−30/40	85.7	0.9	Uragami and Shinomiya (1992)
PMMA-g-PDMS (34/66)	10	PV	40	7.1	4.8	Miyata et al. (1996)
PMMA-g-PDMS (27/73)	10	PV	40	8	5.1	Miyata et al. (1999a)
PMMA-g-PDMS (38/62) ^c	10	PV	40	6.8	3.5	Miyata et al. (1999b)
PTMST	10	TDEV	0/40	77.5	38	Uragami (2010)
Porous PDMS	10	TDEV	0.5	23.1	1,250	Uragami (2008)

^aNormalized permeation rate^bPFA-g-PDMS is 0.2 wt.%^cAnnealing is 120 °C, 2 h

40 mol%, water permeates preferentially from an aqueous solution of 10 wt.% ethanol, whereas membranes with more than about 40 mol% of DMS are ethanol/water selective, as shown in Fig. 2. The change in the ethanol/water selectivity of the PMMA-g-PDMS membranes can be explained by a microphase-separated polymer structure using Maxwell's model and a combined model consisting of both parallel and series expressions. Furthermore, image processing of TEMs allowed the determination of the percolation transition of the PDMS phase at a DMS content of about 40 mol%. These results suggest that the continuity of the PDMS phases in the microphase-separated PMMA-g-PDMS membranes directly affects their ethanol/water selectivity for aqueous ethanol solutions (Miyata et al. 1995, 1996).

In Table 1, the performance of the ethanol-/water-selective polymer membranes is compared. As can be seen in this Table, the addition of PFA-g-PDMS to the PTMSP membrane in PV was very effective, the application of TDEV method to the membrane separation technique was also very interesting for the enhancement of the ethanol/water selectivity for the ethanol/water mixtures, and in particular the application of porous PDMS membrane to temperature-difference controlled evaporation (TDEV) (Uragami 1998, 2005, 2006a, b, 2008, 2010, 2011; Uragami and Shinomiya 1991, 1992; Uragami and Tanaka 1991, 1993, 1994; Uragami et al. 2002; Uragami and Morikawa 1989) was a very excellent performance for the ethanol/water mixtures.

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Alcohol Removal by Membrane Operations

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Synonyms

Alcohol separation by [Membrane Distillation \(MD\)](#); Alcohol separation by [Pertraction](#); Alcohol separation by [Pervaporation \(PV\)](#); Alcohol separation by [Vapor permeation](#)

Biochemical, i.e., fermentative, production of alcohols and other solvents has been increasing significantly in the last years. Recovery and purification of alcohols from dilute aqueous solutions obtained after fermentative solvent production is energy intensive and expensive. For example, conventional distillation is stated to be an efficient alcohol separation technique for the ethanol in concentration range from 10 to 85 wt.% (Huang et al. 2008). The use of membrane operations is however seen as a more cost- and energy-efficient method over conventional distillation in the case

of dilute alcohol solutions (excluding methanol). Especially the use of selective membranes for ethanol or *n*-butanol removal from dilute fermentation broths has gained a lot of interest recently.

Membrane Operations

The most used membrane operations for alcohol removal include separation techniques like filtration, membrane distillation (also known as membrane evaporation), pertraction, pervaporation (PV), and vapor permeation (VP). Micro-, nano-, and ultrafiltration are used in solid-liquid separations mainly as a pretreatment step prior to the alcohol removal. In pertraction, the membrane is placed between fermentation broth and extractant. The membrane passes through the alcohol enabling its extraction, while other components such as nutrients and intermediate products remain in the feed side. In pervaporation and vapor permeation, desired minor compounds from a feed solution are diffused through the hydrophobic membrane and desorbed in the permeate side of the membrane as a vapor which can then be condensed back to the liquid state by, e.g., a condenser (Schäfer and Crespo 2005). Feed solution is in a liquid phase in PV applications and in a vapor phase in VP processes. The driving force, a chemical potential difference of the compounds, is obtained by applying different partial vapor pressures of compound(s) on the opposite sides of the membrane: The feed side is under atmospheric pressure, whereas vacuum or very low pressure is applied in the permeate side. Because only permeated compounds are evaporated in pervaporation, lower energy, capital, and processing costs can be obtained as compared to other separation techniques.

Membranes

Membranes used in alcohol removal are hydrophobic, i.e., organophilic, having preferential permeation for organic compounds instead of water.

Nonporous membranes are used in PV and VP applications, while membrane distillation operations are performed with semipermeable porous membranes. The semipermeable polymeric membranes used mostly are made of polydimethylsiloxane (PDMS). Other used materials include, e.g., polyether block amide (PEBA), polyoctylmethyl siloxane (POMS), polypropylene (PP), polytetrafluoroethylene (PTFE), polytrimethylsilylpropyne (PTMSP), polyvinylidene fluoride (PVDF), and liquid membranes. Ceramic and zeolite membranes are also available. Composite membranes having a porous support layer and a thin separation layer are widely used due to better separation efficiency and membrane stability. Besides a good chemical, mechanical, and thermal stability, membranes should also have high flux and selectivity toward alcohols. Membrane modules can be in the form of flat sheets or plates, spiral wounds, envelopes, or (hollow) tubular modules (Brüschke 2001).

Advantages and Disadvantages

Advantages of membrane operations include the possibility to be used also in the case of azeotropic mixtures and for the separation of volatile organic compounds. In addition, combining the membrane operation with a fermentor as a hybrid process as in situ product removal (ISPR) enables obtaining an increased yield in fermentation and more efficient separation efficiency. Other hybrid processes are typically a membrane operation combined with distillation or with other membrane technique. The main disadvantage in the operation is the fouling tendency of the membrane surface or of the pores inside the membrane, in addition to concentration polarization. Fouling can be reduced by improved membrane module design or operating procedures (Vane 2005).

Industrial Applications

In commercial scale, ethanol is usually first dehydrated by distillation up to the ethanol

concentration of around 92.4 wt% (below the azeotropic point), and further dehydration is done by other separation techniques including, e.g., adsorption by molecular sieves. Especially, pervaporation and vapor permeation are more energy-efficient and promising techniques, but only a few number of pilot- or industrial-scale facilities for alcohol separation are in use, despite the active research going on in laboratory scale. Hence, there is still need for research and development activities to obtain feasible industrial-scale applications.

Cross-References

- ▶ [Alcohol and Water Separation](#)
- ▶ [Butanol-Water Mixtures: Separation by Pervaporation](#)
- ▶ [Ceramic Membranes](#)
- ▶ [Fouling in Membranes](#)
- ▶ [Pervaporation \(PV\)](#)
- ▶ [Polarization in Membrane Operations](#)

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Alcohol Separation by Membrane Distillation (MD)

- ▶ [Alcohol Removal by Membrane Operations](#)

Alginate

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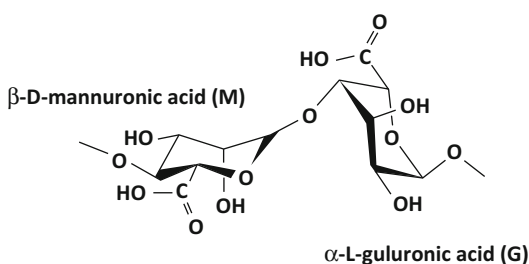
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Alginates are unbranched anionic polysaccharides consisting of 1→4 linked β -D-mannuronic acid (M) and its C-5 epimer α -L-guluronic acid (G) (Fig. 1).

The natural copolymer is an important component of algae such as kelp and is also an exopolysaccharide of bacteria including *Pseudomonas aeruginosa*. The copolymer composition, sequence, and molecular weights vary with the source and species that produce the copolymer. The molecular weights of commercially available sodium alginates range between 32,000 and 400,000 g/mol. The viscosity of alginate solutions increases as pH decreases and reaches a maximum around pH 3–3.5, as carboxylate groups in the alginate backbone become protonated and form hydrogen bonds. The solubility of alginates in water is governed by three parameters, i.e., (a) pH of the solvent, (b) ionic strength of the medium, and (c) the presence of gelling ions in the solvent. To make alginates soluble, it is essential that the pH be above a certain critical value and the carboxylic acid groups be deprotonated. Changing the ionic strength of the medium affects solution properties such as polymer conformation, chain extension, viscosity, and therefore solubility. Alginates gel in the presence of divalent cations such as Ca^{2+} , Sr^{2+} , and Ba^{2+} . It is therefore

necessary to have an aqueous solvent free of cross-linking ions to enable dissolution. The solubility of alginates in organic media requires formation of a tetrabutylammonium (TBA) salt. The solubility of alginates depends strongly on the state of the backbone carboxylic acid groups. Alginic acid with its carboxylic acid groups in their protonated form was not fully soluble in any solvent system examined, including water.

Chemical modification or derivatization of alginates is used as a tool to attain one of two ends, i.e., (a) enhance existing properties (such as improvement of ionic gel strength by additional covalent cross-linking, increase hydrophobicity of the backbone, improve biodegradation, or achieve greater HAP nucleation and growth) or (b) introduce completely new properties otherwise not existing in unmodified alginates (such as afford anticoagulant properties, provide chemical/biochemical anchors to interact with cell surfaces, or bestow temperature-dependent characteristics such as lower critical solution temperature). Alginate derivatization (Pawar and Edgar 2012) includes acetylation, phosphorylation, sulfation, hydrophobic modification, attachment of cell signaling molecules, covalent cross-linking, and graft copolymerization. In particular, amphiphilic alginate derivatives have been synthesized by introducing hydrophobic moieties (e.g., alkyl chains, hydrophobic polymers) to the alginate backbone. These derivatives can form self-assembled structures such as particles and gels in aqueous media and have potential in many drug delivery applications. Alginate derivatives containing cell-adhesive peptides have been gaining significant attraction recently. These derivatives are typically prepared by chemically introducing peptides as side chains, using carbodiimide chemistry to couple via the carboxylic groups of the sugar residues. Since alginate inherently lacks mammalian cell adhesivity, appropriate ligands are crucial to promote and regulate cellular interactions, especially for cell culture and tissue engineering applications. Peptides including the sequence arginine-glycine-aspartic acid (RGD) have been extensively used as model adhesion ligands, due to the widespread presence of integrin receptors for this ligand on



Alginate, Fig. 1 Components of alginates

various cell types. RGD-containing peptides can be chemically coupled to the alginate backbone using water-soluble carbodiimide chemistry.

Alginate is typically used in the form of a hydrogel. Hydrogels are three-dimensionally cross-linked networks composed of hydrophilic polymers with high water content. Hydrogels are often biocompatible, as they are structurally similar to the macromolecular-based components in the body, and can often be delivered into the body via minimally invasive administration. Alginate chelates with divalent cations to form hydrogels. Gel formation is driven by the interactions between G blocks which associate to form tightly held junctions in the presence of divalent cations. In addition to G blocks, MG blocks also participate, forming weak junctions. Thus, alginates with high G contents yield stronger gels.

Chemical and/or physical cross-linking of hydrophilic polymers are typical approaches to form hydrogels, and their physicochemical properties are highly dependent on the cross-linking type and cross-linking density, in addition to the molecular weight and chemical composition of the polymers. The most common method to prepare hydrogels from an aqueous alginate solution is to combine the solution with ionic cross-linking agents, such as divalent cations. The affinity of alginates toward divalent ions decreases in the following order: $\text{Pb} > \text{Cu} > \text{Cd} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Co, Ni, Zn} > \text{Mn}$. Ca^{2++} ; however, it is the most commonly used cation to induce alginate gel formation. Calcium cross-linking of alginates can be performed by two methods. The first is a “diffusion” method, wherein cross-linking ions diffuse into the alginate solution from an outside reservoir. The second is the “internal setting” method, where the ion source is located within the alginate solution and a controlled trigger (typically pH or solubility of the ion source) sets off the release of cross-linking ions into solution. Diffusion set gels are typically made by dropping a Na-alginate solution into a CaCl_2 bath. Internal set gels typically use insoluble calcium salts such as CaCO_3 as a calcium source. The gelation rate is a critical factor in controlling gel uniformity and strength when using divalent cations, and slower gelation

produces more uniform structures and greater mechanical integrity. One critical drawback of ionically cross-linked alginate gels is the limited long-term stability in physiological conditions, because these gels can be dissolved due to release of divalent ions into the surrounding media due to exchange reactions with monovalent cations and the hemostasis promoted by the calcium ions released from the gel that serves as a matrix for aggregation of platelets and erythrocytes. Covalent cross-linking has been widely investigated in an effort to improve the physical properties of gels for many applications, including tissue engineering. However, covalent cross-linking reagents may be toxic, and the unreacted chemicals may need to be removed thoroughly from gels. The inability to dissociate and reform bonds leads to significant elastic deformation. Thermosensitive hydrogels have been widely investigated to date in many drug delivery applications, due to their adjustable swelling properties in response to temperature changes, leading to on-demand modulation of drug release from the gels. When alginate is modified with cell adhesion ligands, the ability of cells to bind multiple polymer chains can lead to long-distance, reversible network formation even in the absence of chemical cross-linking agents. Cells added to an RGD-modified alginate solution form a uniform dispersion within the solution, and this system subsequently generates the cross-linked network structure via specific receptor-ligand interactions without using any additional cross-linking molecules. In contrast, cells added to non-modified alginate solutions aggregate and form a nonuniform structure, due to the dominance of cell-cell interactions in that system. This gelation behavior is shear reversible and can be repeated multiple times. Once the gel structure is broken down by applying shear forces, cross-linked structures are recovered within a few minutes. This behavior is governed by the weak and reversible ligand-receptor interactions in the system. This system might be ideal for cell delivery in tissue engineering because a gel can flow like a liquid during injection into the body but solidify once it is placed in the body.

Large pellets (greater than 1.0 mm in diameter) are conventionally prepared using a simple

syringe or pipette. Droplets of sodium alginate solution are extruded into a divalent cross-linking solution, and pellets formed are then allowed to cure in the cross-linking solution (varying from a few minutes to hours), rinsed with water, and air-dried. Micropellets (less than 0.2 mm in diameter) can be prepared using atomization, emulsification, and coacervation methods.

Polysaccharides undergo hydrolytic cleavage under acidic conditions. The mechanism of acid hydrolysis of the glycosidic bond involves three steps: (1) protonation of the glycosidic oxygen to give the conjugate acid; (2) heterolysis of the conjugate acid forming a nonreducing end group and a carbonium-oxonium ion; and (3) rapid addition of water to the carbonium-oxonium ion, forming a reducing end group. The enzymatic degradation of alginates by lyase occurs by a β -elimination mechanism resulting in unsaturated compounds. The mechanism of β -elimination involves abstraction of the proton at the C-5 position, which is enhanced by the electron-withdrawing effect of the carbonyl group at C-6 position. Alginates chain degradation can occur also at neutral pH values in the presence of reducing compounds such as hydroquinone, sodium sulfite, sodium hydrogen sulfide, cysteine, ascorbic acid, hydrazine sulfate, and leucomethylene blue that also caused degradation in alginates. The mechanism of degradation involves the formation of a peroxide leading to free radical creation, which eventually causes breakdown of the alginate chain.

Alginate is inherently nondegradable in mammals, as they lack the enzyme (i.e., alginase) which can cleave the polymer chains, but ionically cross-linked alginate gels can be dissolved by release of the divalent ions cross-linking the gel into the surrounding media due to exchange reactions with monovalent cations such as sodium ions. An attractive approach to make alginate degradable in physiological conditions includes partial oxidation of alginate chains. Slightly oxidized alginate can degrade in aqueous media, and these materials have demonstrated potential as a delivery vehicle of drugs and cells for various applications. Alginate is typically oxidized with sodium periodate.

The chemical and physical properties of alginates resulted in many commercial applications (Goh et al. 2012; Lee and Mooney 2012):

- (i) Food and beverage industry (stabilizers, thickeners in the preparation of drinks, ice cream, and jelly; encapsulation material of yeast cells in ethanol production)
- (ii) Pharmaceutical industry (encapsulation material in cell culture and transplantation, mold in dental impression material, adhesive agent and sustained release in tablets, hemostatic and absorbent in wound dressing)
- (iii) Other industries (adhesive agent and filler in paper industry, stabilizer and suspending agent in paint industry)

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Aligned Carbon Nanotube

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Synonyms

A-CNT; Horizontally aligned carbon nanotube;
Vertically aligned carbon nanotube

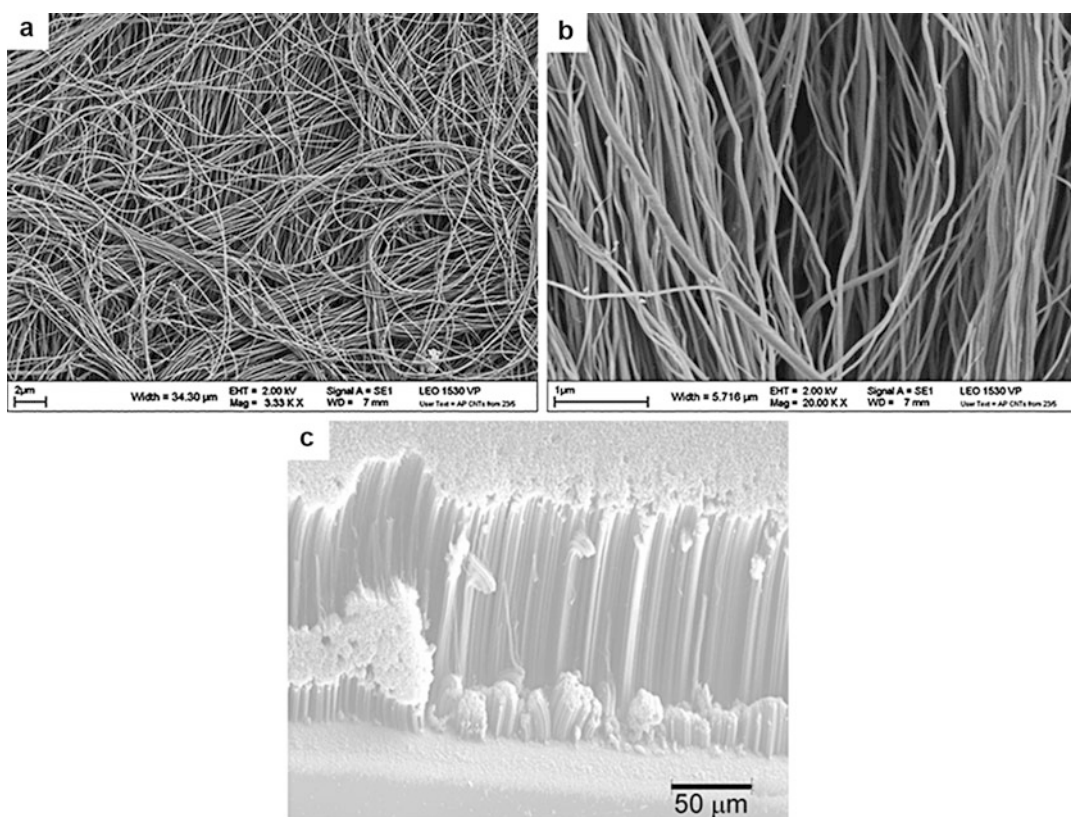
Main Text

Carbon nanotubes (CNTs) are allotropes of carbon in which the carbon atoms form a hexagonal sheet of sp^2 bonds (analogous to graphite) which is seamlessly rolled up into a cylinder that can be microns long but is only nanometers in diameter (Yamamoto et al. 2008). Following typical synthesis procedures, CNTs exist as a tangled web of randomly oriented fibers. For many applications, the CNTs are required to be aligned with either horizontal or vertical alignment (Fig. 1).

Horizontally aligned CNTs are of particular importance in the generation of field effect transistors and conductive wires based upon CNTs. CNTs can be horizontally aligned via a range of processes including spin coating, filtering, magnetic field alignment, and drying-induced and chemical vapor deposition (CVD) (Dai 2001; Joselevich

et al. 2008). Horizontal CNTs can form a dense, flexible, stable mat (called a “bucky paper”) which can potentially be used as a membrane as the space between the CNTs is generally quite small (<50 nm) (Dumée et al. 2010; Sears et al. 2010).

Vertically aligned CNTs can be prepared via the CVD growth of CNTs on pre-patterned substrate supported catalyst nanoparticles. Vertically aligned CNTs produced via this method have been grown greater than 1 mm in length (Joselevich et al. 2008). Alignment is enhanced via the use of a strong electric field such as in plasma-enhanced CVD. Vertical alignment is of importance in the fields of field emission, chemical sensing, and CNT nanofiltration membranes (Endo et al. 2008; Shearer et al. 2012). CNT nanofiltration membranes are of particular interest as molecular dynamics simulations have shown that water can flow through CNTs at a



Aligned Carbon Nanotube, Fig. 1 SEM image CNTs produced via CVD showing (a) randomly entangled, (b) horizontally aligned, and (c) vertically aligned

remarkable rate (Hummer et al. 2001), while the flow of contaminants is restricted by the nano-size of the CNT inner pore (~ 1 nm). The fabrication of such a membrane required vertically aligned CNTs, encased within an impermeable matrix such that flow can only occur through the CNT inner pore. This is experimentally quite difficult, but a few reports with promising results have been published (Majumder et al. 2005; Holt et al. 2006; Wu et al. 2010).

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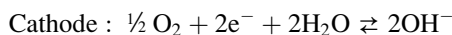
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Alkaline Fuel Cells (AFCs)

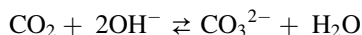
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Alkaline fuel cell (AFC) is a fuel cell type which utilizes alkaline electrolyte, usually potassium hydroxide. It consumes hydrogen and oxygen producing only water, heat, and electricity. Depending on a concentration of potassium hydroxide, AFC can operate at temperatures between 60 °C and 250 °C. The fuel cell reactions are as follows:



The main ionic charge carriers are OH^- ions which mitigate from the cathode to the anode. Water is formed at the anode side and has to be removed from the system in order to prevent KOH dilution. The AFC has improved cathode performance compared to acidic fuel cells due to more favorable oxygen reduction reaction kinetics. For this reason, AFC can achieve higher efficiency, i.e., higher voltage at comparable current densities than other fuel cell types. It has very long operating life time, e.g., 15,000 h have been demonstrated (Cifrain and Kordesch 2003). Furthermore, alkaline conditions allow application of nonprecious metal catalysts which could reduce significantly the material costs of this fuel cell. One of major disadvantages of AFC is its low CO_2 tolerance due to formation of carbonates according to:



The carbonates have low solubility in strong alkaline environments forming crystals, capable of

blocking of electrolyte pathways. The low CO₂ tolerance and the application of liquid electrolyte are two main hurdles for the broader commercialization of these systems. However, due to its high efficiency and high power density, AFC found applications in aerospace industry, e.g., they were employed on the Apollo missions as well as on the Space Shuttle orbitals. For other examples of developed AFC systems, please see Cifraín and Kordesch (2003) and Gülzow (2012).

Hydrogen and oxygen gases in the AFC are separated by a membrane. Usually permeable membranes also called diaphragms have been used (Gülzow 2012). A common diaphragm material up to 1980s was asbestos which due to health and environmental concerns is nowadays abandoned. Alternative materials are different polymer materials like porous polyethylene plates, nonwoven polypropylene, and similar. Potassium hydroxide electrolyte wets the diaphragm pores in order to ensure its ionic conductivity. For a good fuel cell performance, the electrolyte resistance induced by diaphragm has to be minimized. This resistance is influenced by the thickness of the diaphragm material, its pore size and tortuosity, and the KOH concentration. Since liquid electrolyte causes some practical problems in AFC usage, new developments go into direction of alkaline polymer electrolyte membranes which, in addition to separation, possesses ionic conductivity in the absence of liquid electrolyte. Currently there is no long-term stable membrane functioning without a liquid electrolyte phase.

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Alkane and Alkene Separation by Membrane Operations

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Alkenes (e.g., ethene, propene, butadiene, and butenes isomers) are extremely important building blocks in petrochemical industries with many derived chemicals and polymers. Traditionally, alkenes are recovered from alkene/alkane mixtures produced by cracking hydrocarbon feedstocks (e.g., ethane, LPGs, and naphtha). Alkene/alkane separations (e.g., separation of ethene/ethane, propene/propane, and butadiene/crude C₄) are traditionally performed on a massive scale by distillation, which are extremely energy intensive due to these components' close volatilities. For example, propene/propane separation was credited to be the most energy intensive commercially practiced distillation (Jarvelin and Fair 1993).

Membrane gas separations, among other competing alternatives (i.e., adsorptive separation and chemical absorption), can be used to either retrofit or replace existing distillation columns to make commercial alkene/alkane separations more energy efficient. Compared with well-developed membrane gas separations such as air separation, membrane-based alkene/alkane separation is more challenging. The feeds are highly condensable and usually under high pressure (or in liquid state), requiring that membrane materials must be sufficiently robust without being plasticized. Among alkene/alkane separations, ethene/ethane and propene/propane are most extensively studied with membranes. Conversely, membranes are less commonly considered for separations of C₄ and heavier alkene/alkane mixtures due to their much lower diffusivities and correspondingly unattractive productivities. Membrane separations are based on differences in how fast the penetrants diffuse through the membrane (i.e., diffusion selectivity) and/or how much they sorb in the membrane (i.e., sorption selectivity). For example, propene molecule is slimmer than propane

molecule. Remarkable propene/propane diffusion selectivity is possible for materials with rigid structures and properly tailored ultramicropores. Additionally, propene is slightly polar and a limited (<10) propene/propane sorption selectivity may be achieved with polar materials (e.g., cationic zeolites with high Al/Si ratio).

Membranes for alkene/alkane separations can be categorized into two classes: membrane separations based on sorption-diffusion and others based on facilitated transport. The majority of membranes in the first category achieve the separation relying on diffusion selectivity. Polymer membranes, despite their excellent scalability, are incapable of offering attractive alkene/alkane selectivity without significantly compromising their permeability due to the permeability-selectivity trade-off (Burns and Koros 2003). Additionally, uncrosslinked polymer membranes may be plasticized with high-pressure alkene/alkane feeds, resulting in significant selectivity loss. On the other hand, membranes derived from more rigid molecular sieving materials (e.g., zeolites, metal-organic frameworks [MOFs], zeolitic imidazolate frameworks [ZIFs], and carbon molecular sieves [CMS]) can offer simultaneously high permeability and selectivity. However, fabrication of molecular sieve membranes is usually difficult and many technical challenges must be solved to deliver such performance economically on a large scale. Among molecular sieve membranes, CMS membrane is the most promising as it can be conveniently realized in the scalable hollow fiber geometry by pyrolyzing polymer precursor hollow fibers. A compromise to address the limitations of both polymer membrane and molecular sieve membrane is mixed-matrix membrane (Adams et al. 2013), which are formed by dispersing molecular sieve particles/platelets in polymer matrices. Selectivity and/or permeability of mixed-matrix membranes may be substantially enhanced over the polymer matrices and in the meantime, the membrane can still be inexpensively processed into hollow fibers (Zhang et al. 2014).

Facilitated transport membrane is another class of membrane studied for alkene/alkane

separations (Faiz and Li 2012). Alkene transport in such membranes is assisted by carriers (e.g., Ag^+ ions) that reversibly react with alkenes through π -complexation. Amazing alkene permeability and alkene/alkane selectivity can be achieved in facilitated transport membranes at the same time. Nevertheless, the carriers may be irreversibly deactivated by certain impurities (e.g., hydrogen, hydrogen sulfide, and acetylenes) in the feed, resulting in permanent loss in both alkene permeability and alkene/alkane selectivity. While in some cases membrane performance may be partially recovered by periodically recharging the carrier, such approach may not be practical for large-scale applications.

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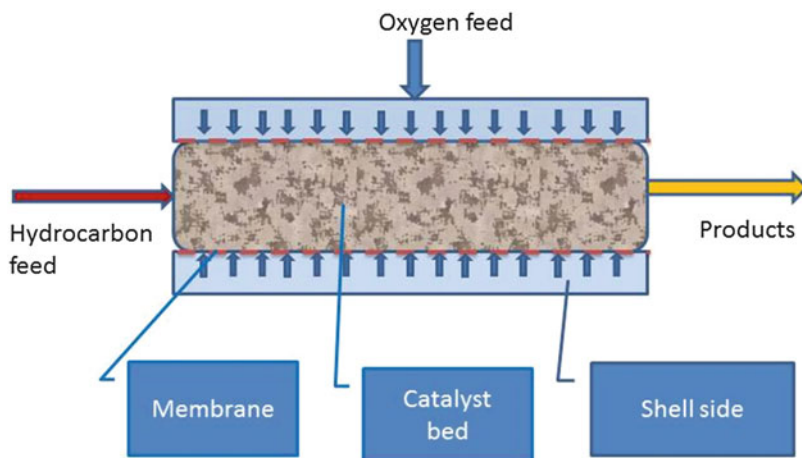
Alkene Oxidative Dehydrogenation by Membrane Reactor

Miguel Menendez

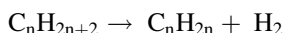
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Alkanes are converted to olefins in the chemical industry because of the high demand of polyolefins, such as polypropylene or polybutadiene, and

Alkane Oxidative Dehydrogenation by Membrane Reactor,
Fig. 1 Scheme of a membrane reactor for the selective oxidation of hydrocarbons with a distributed feed of oxygen

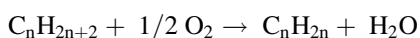


also because olefins are the starting materials for many other chemicals. These reactions can be represented as



A common characteristic of these reactions is the achievable conversion being limited by thermodynamic equilibrium. Two options to increase the conversion are

- Using a membrane reactor where H_2 is removed from the reactor. This will increase the achievable conversion according to the Le Chaterlier's principle. Any material which can remove hydrogen selectively can be used, but Pd and Pd alloys are the most employed. The preparation of this kind of membranes has been widely described (Basile and Gallucci 2011).
- Adding an oxidizing agent (e.g., oxygen) to the reaction, in order to form water instead of hydrogen, the resulting reaction would be:



This approach has the advantage of being thermodynamically favored but has the problem that simultaneous formation of carbon oxides reduces the selectivity.

A way to improve the selectivity is to use a membrane reactor, where the membrane

distributes oxygen along a packed bed of catalyst. This improvement is based on the *favorable effect of low oxygen partial pressure* on the selectivity. In fact, for many catalysts the observed reaction order respect to oxygen for the above reaction is lower than for the formation of CO and CO_2 . This observation implies that low partial pressure of oxygen increases the selectivity to olefins.

This general principle has been applied for the oxidative dehydrogenation of ethane, propane, and butane, with successful results in all cases (Coronas and Santamaría 1999). Details of the results obtained with membrane reactors with propane and butane (oxidative dehydrogenation and oxidation to maleic anhydride) are described in specific chapters.

A general scheme of a membrane reactor for this kind of reactions is shown in Fig. 1.

The oxygen containing feed is usually introduced through the shell side. A porous membrane distributes this oxygen along the catalyst bed, keeping a low partial pressure of oxygen in all the beds. A feed containing the hydrocarbon is fed to the tube side, i.e., to the catalyst bed. The reaction products are removed at the exit of the catalyst bed.

As an alternative to porous membranes, dense ceramic membranes can provide an additional advantage: the separation of oxygen-nitrogen mixtures (Hashim et al. 2011). This would decrease the cost of oxygen separation.

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Alumina Membranes

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Alumina membranes are membranes made of high-purity (mostly >97 %) aluminum oxides (alumina). They belong to the categories of ceramic membranes and in most cases, microfiltration and ultrafiltration membranes. Pure alumina membranes are predominant in all kinds of commercial ceramic membranes, and most other commercial ceramic membranes, if using other materials as the separation coating, are based on alumina membrane support.

Advantages and Disadvantages

Alumina membranes are chemically inert and mechanically strong, and also thermally stable, therefore they can be used under very harsh conditions such as aggressive chemical environments and elevated temperatures, making them versatile in various industrial processes. Their strong mechanical properties allow them to be operated under high pressures and high feed flow rates to achieve high productivity and to tolerate high solid contents in the feed.

The high fabrication cost is a major obstacle for alumina membranes to expand its market share. Although alumina is widely available, the complicated fabrication process and high energy consumption for sintering lift significantly the total

membrane cost, making it about one order of magnitude higher than its polymeric counterparts. However, because of much longer lifetimes and higher fluxes of alumina membranes, the long-term operating cost of alumina membrane plants is comparable with polymeric membrane plants, no mention there are many scenarios in which only alumina/ceramic membranes can be used.

Membrane Designs and Fabrication

Most alumina membranes use asymmetric membrane architectures. Coarse alumina particles are used for the supporting layer to provide mechanical strength, and the transport resistance in this layer is usually low due to its big pore size; fine alumina particles are coated on top of the support to form a thin separating layer to reach desired pore sizes and high fluxes; and depending on the pore size difference between the top and the supporting layer, one or few transition layers might be used between the top and supporting layers to avoid coating defects and to increase adhesion between layers.

Alumina membranes may adopt a tubular shape, plate shape, or monolithic multichannel design. The latest is the most commonly used design in industry because it provides higher membrane area per unit volume, therefore reduces the size of the separation plant and operating costs. Some commercial products can achieve an area to volume ratio of $800 \text{ m}^2/\text{m}^3$ with the monolithic design, which is comparable with spiral wound polymeric membrane modules.

Fabrication of alumina membranes usually involves several forming and sintering steps due to their multilayer asymmetric membrane architectures, and the total production process is often longer than 1 week. The supporting layer can be formed by extrusion (for tubular or monolith designs) or by pressing (for plate or disk designs), followed by partial sintering at a high temperature (up to 1600°C) to achieve a high strength and porous structures. Transition layers and the top layer then can be coated on the support, also followed by sintering after each coating. Depending on the pore size, two types of alumina

could be used for the top layer coating: for microfiltration membranes whose pore size is larger than 100 nm, α -alumina is used; for ultra-filtration membranes whose pore size is smaller than 100 nm, γ -alumina or a mixture of α and γ types are often used.

There are also other fabrication techniques that can produce unique alumina membranes, for example, the anodic alumina membranes that have straight cylindrical pores and asymmetric alumina membranes made by single-step phase inversion/sintering methods. These membranes have shown good potential in filtration but have not been widely accepted as a feasible replacement of conventional alumina membranes yet.

Applications

Alumina membranes are widely used in water and wastewater treatment, pharmaceuticals, food processing, chemical processing, and others. Production of drinking water and wastewater treatment are the most important applications, which occupy about half of the market share of alumina membranes. The stable pore structure of alumina membranes even under high pressures and abrasive conditions guarantees constant quality of the permeate and makes it preferable in the scenarios where quality control is crucial, such as in drinking water production and food industry. And the natural hydrophilic surface of alumina offers better anti-fouling property than polymeric membranes; therefore its usage in wastewater treatment is expanding rapidly; and in some other heavy-duty filtration processes such as treating produced water from oil fields, alumina membranes have been dominant.

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Aluminum (III) Oxide Porous Membranes or Alumina Porous Membranes

- [Al₂O₃ Porous Membranes](#)

Americium Separation by Membrane Operation

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Americium (Am) is the first among the transplutonium elements, produced in nuclear reactors in large quantities. Due to long half-lives of its isotopes ($t_{1/2}$ of ^{241}Am , 432 y; ^{243}Am , 7370 y), this element can have long-term hazards to the environment if not separated from the radioactive wastes before their disposal. Separation of Am mostly involves solvent extraction-based methods involving specially designed ligands for Am uptake. Membrane-based separation has been used for Am separation using pressure-driven techniques such as nanofiltration, facilitated by complexation (Favre-Réguillon et al. 2007). However, selectivity factors in such separation systems are not encouraging. Liquid membrane-based separation systems, with Am-specific carrier extractants, are reported to give better decontaminations.

Some of the first studies on Am transport using supported liquid membranes include the work of Danesi, who used CMPO (carbamoylmethylphosphine oxide) as the carrier extractant (Danesi et al. 1983). Feed solutions containing LiNO_3 resulted in highly encouraging

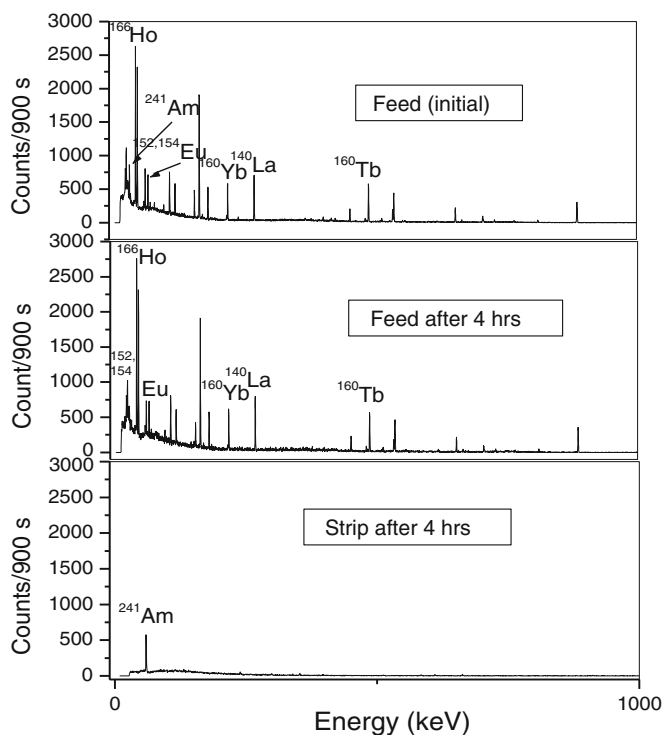
Am transport rates which were significantly affected in the presence of nitric acid in the feed, attributed to the cotransport of nitric acid. The Am transport rates could be improved by using a second membrane in parallel containing Primene JM-T as the carrier extractant for selective transport of nitric acid (Chiarizia and Danesi 1987). In another study, triphosphine trioxide extractants have been employed for Am(III) transport from NaNO_3 solutions with encouraging results (Cristau et al. 1999). Other extractants such as tetra-alkyl malonamides and diglycolamides have shown comparable or even better transport efficiency for Am as compared to CMPO. Malonamides such as DMDBTDMA (N,N'-dimethyl-N,N'-dibutyltetradecyl malonamide) and DMDOHEMA (N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide) are reported to be quite efficient for Am(III) transport (Sriram et al. 2000; Patil et al. 2013). TODGA (N,N,N',N'-tetraalkyldiglycolamide) has been found to be one of the best carriers for Am(III) transport due to significantly lower acid cotransport as compared to CMPO or malonamides (Ansari et al. 2009).

TODGA-based hollow-fiber supported liquid membrane system has been successfully used in a mini pilot-scale processing of synthetic high-level waste (Ansari et al. 2011). A series of studies have indicated that the diluents play a significant role in Am transport rates which are mainly due to two factors: (i) nature of the extracted species and (ii) diffusivity of the extractable complex which is based on the viscosity of the medium (Panja et al. 2012).

Am(III) separation of trivalent lanthanides has also been studied using various Am(III) selective extractants such as Cyanex 301 (Hoshi et al. 2000), BTP (Geist et al. 2005), etc. In one of the early reports on Am(III)–Eu(III) separations using liquid membranes (Novikov and Myasoedov 1987), almost no transport of Am(III) was observed while effecting complete quantitative Eu(III) transport using a feed composition of 0.01 M DTPA, 0.5 M citric acid, 0.5 M NaNO_3 at pH 2.9, and 1 M HDEHP as the carrier extractant. Cyanex 301 has been used for highly selective Am(III) transport of a feed also containing several trivalent lanthanide ions (Fig. 1; Bhattacharyya et al. 2006). Oxidation

Americium Separation by Membrane Operation,

Fig. 1 Gamma ray spectrum of the feed and receiver solutions measured using HPGe detector (Bhattacharyya et al. 2006)



to the +4 and +6 states reportedly enhanced Am transport rates due to higher extraction efficiencies of these ions. Tri-*n*-octylamine containing liquid emulsion membrane (LEM) systems has been used for the transport of Am(IV) which was done using phosphotungstate (Myasoedov et al. 1990). In another report (Mikheeva et al. 1994), the transport of hexavalent Am by electrochemical oxidation followed by simultaneous transport using HDEHP as the carrier.

There are several reports on the Am(III) recovery from acidic feeds using liquid emulsion membranes (LEM) using extractants such as HDEHP, PC-88A, and TODGA as well. Usually, the LEM methods are much faster as compared to the SLM-based separation methods which are due to highly dispersed globules containing the internal phase as the strippants present in the emulsion which effect rapid mass transfer. In a recent study, multifunctional ligands such as the calixarenes anchoring diglycolamide functional groups have shown improved transport behavior as compared to the simple extractants (Ansari et al. 2013). The liquid membrane methods with lower flux as compared to the solvent extraction methods can be used for pre-concentration and separation of Am from dilute solutions including environmental samples and radioactive wastes.

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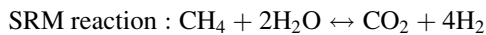
Ammonia Decomposition in Catalytic Membrane Reactors

Toshinori Tsuru

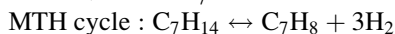
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Recently, NH_3 has been proposed as a H_2 carrier in a promising solution that would bypass the intractable issues related to H_2 storage and delivery, since NH_3 has a high hydrogen storage capacity of 17.6 wt.% and can be easily stored and transported in liquid form under mild conditions. NH_3 decomposes to H_2 , which produces only H_2O after combustion, and N_2 , which is not a greenhouse gas; in other words, NH_3 is a CO_x -free H_2 carrier. Another class of a hydrogen carrier is an organic hydride such as cyclohexane (CH) and methylcyclohexane (MCH). In dehydrogenation reaction, CH and MCH reversibly produce benzene (BEN) and toluene (TOL), based on the equilibrium reaction, respectively, while BEN and TOL are re-hydrogenated into CH and MCH, respectively. Methylcyclohexane-toluene-hydrogen (MTH cycle) and cyclohexane-benzene-hydrogen (CBH cycle) need reversible and highly selective conversion to sustainable use. Therefore, the advantages of NH_3 mentioned above make the NH_3 -mediated hydrogen economy extremely attractive and promising. Other H_2 carriers, such as methanol, dimethyl ether, etc., inevitably cause end-user CO_2 emissions, since they are carbonaceous compounds and on-board CO_2 capture is not feasible.

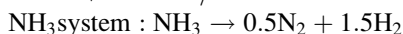
As shown in the following equations, another advantage of NH_3 -energy systems is the low heat of reaction. Approximately 30 kJ is required for one mole of produced H_2 in NH_3 system, which is lower than in MTH cycle (70 kJ) and steam reforming of methane (SRM) (40 kJ).



$$\Delta H = +164.5 \text{ kJ/mol}$$



$$\Delta H = +204.6 \text{ kJ/mol}$$

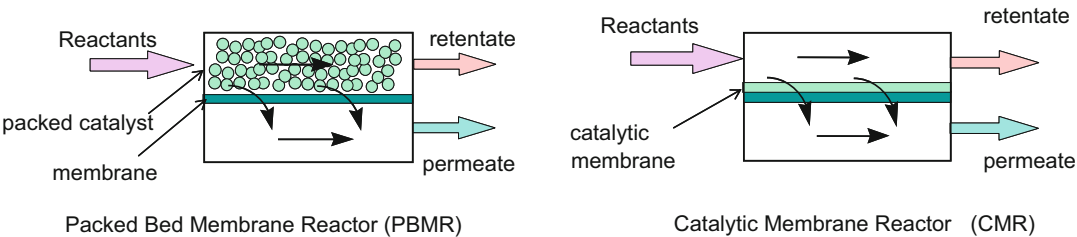


$$\Delta H = +46 \text{ kJ/mol}$$

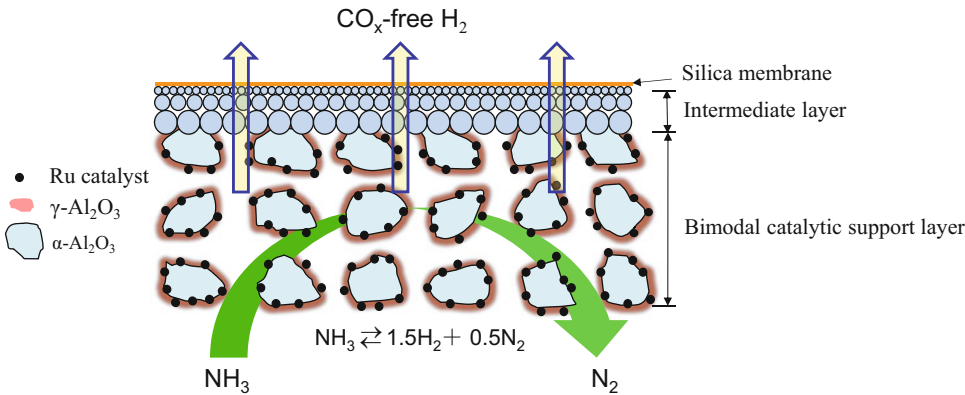
Membrane reactors can be categorized based on configuration of catalysts as packed type membrane reactor, fluidized membrane reactor, and catalytic membrane reactor. As shown in Fig. 1, packed bed membrane reactors consist of catalysts for reaction as well as membranes for separation. Both catalyst particles and membranes are packed into one unit, but reaction and separation occur separately. On the other hand, catalytic membranes have catalytic activity as well as separation ability in one membrane. Zeolite membranes such as ZSM-5 and TS-1 are inherently catalytically active, while another type of catalytic membrane is a silica hydrogen separation membrane on catalytically active support which can be prepared using catalytically active powders such as nickel oxides or impregnation of Ni-catalyst inside porous α -alumina supports (Tsuru et al. 2004).

Membrane reactors combining a catalytic reaction with the separation process into a single unit offer an ideal device to produce H_2 from NH_3 efficiently, where enhanced NH_3 conversion and high-purity CO_x -free H_2 can be simultaneously obtained by applying a hydrogen separation membrane. Ru is reported the most active catalyst for ammonia decomposition and is supported on porous carbon such as carbon nanotubes (CNT) with supporting catalysts such as potassium (K). To date, only a few studies have reported membrane reactors for NH_3 decomposition in a packed bed Pd membrane reactor, and improved NH_3 conversion was obtained after H_2 extraction.

Another class of membrane reactor is a catalytic membrane reactor. Figure 2 shows a schematic bimodal catalytic membrane reactor (BCMR) (Li et al. 2013). This new type of membrane reactor had a configuration that consisted of a silica separation layer and a bimodal catalytic support ($\text{Ru}/\gamma\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$). The impregnation of $\gamma\text{-Al}_2\text{O}_3$ into an $\alpha\text{-Al}_2\text{O}_3$ membrane support to

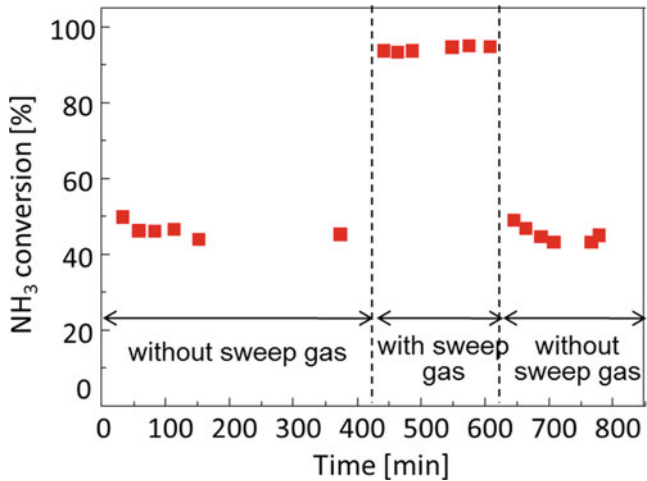


Ammonia Decomposition in Catalytic Membrane Reactors, Fig. 1 Configuration of membrane reactors



Ammonia Decomposition in Catalytic Membrane Reactors, Fig. 2 Schematic diagram of the proposed bimodal catalytic membrane reactor for CO_x-free H₂ production via NH₃ decomposition (Li et al. 2013)

Ammonia Decomposition in Catalytic Membrane Reactors, Fig. 3 Bimodal catalytic membrane reactor performance for NH₃ decomposition at 450 °C (Li et al. 2013)



form a bimodal support is expected to effectively improve catalytic membrane reactor performance, since the bimodal structure contains both mesopores and macropores, which results in

improved catalytic activities by mesopores and high gas diffusivity by macropores.

Figure 3 shows an example of enhancement of conversion for the BCMR performance for NH₃

decomposition at 450 °C. During the initial 250 min without sweep gas, a NH₃ conversion was 45 %. When N₂ sweep gas was applied to the permeate stream of the membrane reactor, NH₃ conversion was significantly enhanced from 45 to 95 % after the selective H₂ extraction. NH₃ decomposition rate is strongly inhibited by the presence of H₂, particularly at a high pressure. Therefore, the highly enhanced NH₃ conversion can be ascribed to the improved kinetics from H₂ extraction in the BCMR.

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Amorphous Fluoropolymers

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Synonyms

Fluorinated polymers; Fluoroplastics; Noncrystalline

Amorphous fluoropolymers are noncrystalline synthetic polymers where the hydrogen atoms of the backbone have been partially or completely replaced by fluorine atoms. While common fluoroplastics are semicrystalline, the number of commercial amorphous perfluoropolymers is relatively limited (Scheirs 2001).

In fluorinated polymers the crystallinity, characteristic of perfluorocarbon –CF₂CF₂– units, can be reduced by incorporation of monomers with pendant side groups, like hexafluoropropene or perfluorovinyl ethers, which disrupt the regularity

of the polymeric sequences and increase the intermolecular distances. The complete suppression of the crystallinity is, instead, more easily achieved by introduction of elevated percentage of cyclic monomeric units; by following this strategy, new families of amorphous glassy perfluoropolymers (Teflon[®] AF, Cytop[®], and Hyflon[®] AD whose structures are reported in Fig. 1) were developed and commercialized starting from the late of 1980s (Merkel et al. 2006).

The cyclic groups, present in each of these three structures, hinder efficient chain packing, thus preventing crystal formation and yielding completely amorphous polymers with a glass transition (T_g) tunable but always sensibly above room temperature (from 95 °C of Hyflon[®] AD40 to 240 °C of Teflon[®] AF2400).

Teflon[®] AF, Cytop[®], and Hyflon[®] AD combine the properties typical of perfluorinated semicrystalline materials (high thermal and chemical resistance, low dielectric constant, low surface energy) with new peculiar properties imparted by the amorphous structure such as the high solubility in fluorinated solvents and excellent transparency across a broad wavelength range (from UV to near IR). Furthermore, the high chain stiffness imparted by the cyclic units leads to a difficult packing of the chain segments with the consequent formation of nano-voids which are responsible for the high gas diffusion of these polymers. Gas separation membranes, pellicles for microlithography, protective coatings, dielectric layers for organic and electronic and plastic optical fibers are the most important applications of these glassy perfluoropolymers.

Other two important families of amorphous fluoropolymers, in this case displaying a T_g value below room temperature, are perfluoropolyethers (PFPEs) and fluorinated elastomers. The former (Fig. 2), obtained by means of different manufacturing technologies (Rizvi Syed 2009; Marchionni et al. 1996), are low molecular weight polymers containing etheric oxygen atoms in the backbone which make the chains extremely flexible so preventing the formation of crystalline phases.

These synthetic fluids display extremely low T_g, even below –100 °C. They find applications

Amorphous**Fluoropolymers,**

Fig. 1 Structure of three commercial amorphous glassy perfluoropolymers

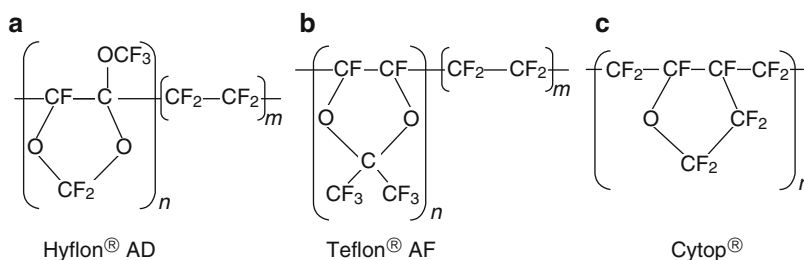
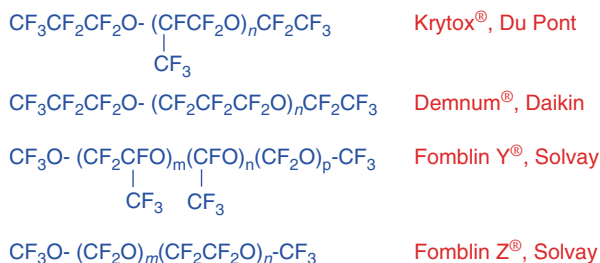
**Amorphous****Fluoropolymers,**

Fig. 2 Structure of the four most important commercial perfluoropolyethers



as lubricants for extreme conditions (high temperatures, high pressure, presence of aggressive chemicals), as testing and heat transfer fluids in electronic, and as inert solvents. PFPEs containing functional-end groups can be used as building blocks for the synthesis of two-phase materials (partially fluorinated, partially hydrogenated), surface treatment agents, and surfactants. Few applications in the field of membranes are known for PFPEs (Chaouk et al. 2001).

Fluorinated elastomers (Moore 2006) are cross-linked amorphous polymers with T_g below room temperature. They are generally obtained by copolymerization of at least two of the following monomers: tetrafluoroethylene, vinylidene fluoride, hexafluoropropene, and perfluorovinyl ethers. Fluorosilicone elastomers, i.e., fluorochemically modified polysiloxanes, are another important class of fluorinated elastomers. Fluoroelastomers show extreme resistance to high temperatures and to a variety of aggressive fluids. They exhibit excellent resistance to oils, solvents, acids, alkalis, and ozone over a wide temperature range (-30°C to 250°C) and, therefore, they are suitable for aggressive environments and severe conditions. No relevant industrial applications in the field of membranes are known.

Cross-References

- [Gas Separation](#)
- [Glass Transition Temperature \(\$T_g\$ \)](#)
- [Hyflon® AD](#)

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Amorphous Perfluoropolymers

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Synonyms

Fully fluorinated polymers; Noncrystalline

Amorphous perfluoropolymers are noncrystalline fully fluorinated synthetic polymers composed exclusively by carbon, fluorine, and oxygen atoms. The most relevant product family for membrane applications is represented by the glassy amorphous perfluoropolymers containing dioxole groups (Teflon[®] AF, Hyflon[®] AD, and Cytot[®]) which display a glass transition above room temperature (Merckel et al. 2006). Perfluoropolyethers and perfluorinated elastomers are, instead, the two most important families of amorphous perfluoropolymers with a glass transition below room temperatures. Perfluoropolyethers (Marchionni et al. 2006; Sanguineti et al. 1995) are a class of synthetic lubricants characterized by extremely low T_g, also below −100 °C. They find applications as lubricants for extreme conditions (high temperatures, high pressure, presence of aggressive chemicals), as heat transfer fluids and as inert solvent (they are good solvent for the glassy amorphous perfluoropolymers). The commercially available PFPEs include Krytox[®], Fomblin[®], and Demnum[®]. Perfluoroelastomers (Moore 2006), also referred to as FFKM elastomers, are amorphous cross-linked polymers obtained by copolymerization of tetrafluoroethylene with hexafluoropropene and/or perfluorovinyl ethers which effectively disrupts the crystallinity imparted by the TFE segments (Marshall 1997). Perfluoroelastomers are characterized by improved thermo-oxidative stability and oil resistance (compared with VDF-based elastomers) for extreme industrial and military applications. Unlike the glassy amorphous perfluoropolymers, no relevant industrial membrane applications for perfluoropolyethers and for perfluoroelastomers are known.

Cross-References

- Glass Transition Temperature (T_g)
- Hyflon[®] AD

References

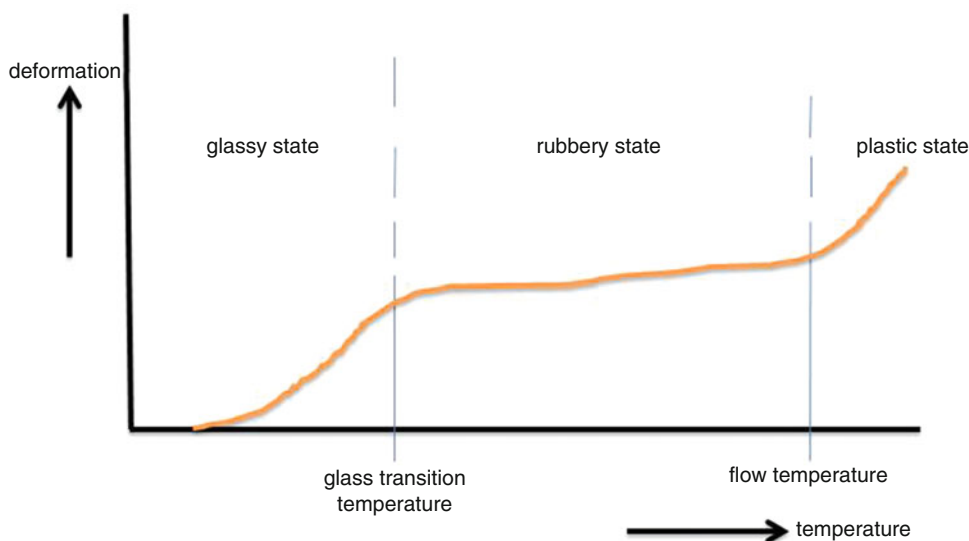
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Amorphous Polymers and the Amorphous Region

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Polymers consist of the large molecules (polymer chains). An arrangement of these chains in the bulk polymer is given by their chemical composition, spatial orientation (e.g., an isotactic vs atactic polypropylene), molecular weight, and processing conditions (e.g., a cooling rate). Based on these factors, bulk polymers show an amorphous or partially crystalline (semicrystalline) phase state. In the amorphous state, an ordering of the (entangled) polymer chains is random. The amorphous polymer does not include a long-range order, but it is characterized by the existence of some regularity on a short-range order. As a consequence of it, an



Amorphous Polymers and the Amorphous Region, Fig. 1 Thermomechanical curve of an amorphous polymer

X-ray diffraction provides a diffuse ring only (a set of discrete rings is typical for well-ordered structures). If the amorphous polymer is exposed to a gradually increased temperature, it passes from a glass (hard and rigid) to a rubber (soft and flexible) and finally to a molten consistency. Boundaries between the glass/rubber and rubber/molten consistency are given by a glass transition temperature (T_g) and flow temperature, respectively (see a thermomechanical curve of an amorphous polymer, Fig. 1).

The glass transition temperature of the polymer is also an important indicator of its application temperature region (e.g., polydimethylsiloxane ($T_g = \text{ca } -120^\circ\text{C}$) is rubbery and polystyrene ($T_g = \text{ca } +100^\circ\text{C}$) is a glassy polymer at room temperature). A character of the main backbone (flexible/rigid), its substitution (small vs bulk substituents), and a level of molecular (chain) interactions (e.g., van der Waals forces vs hydrogen bonds) are important factors influencing the position (value) of this transition. A flexibility of the chains (or segments) of an amorphous polymer is restricted at temperatures below its T_g . Under heating, molecular interactions (secondary forces) are disrupted, and a free volume among more flexible chains increases (Fig. 2).

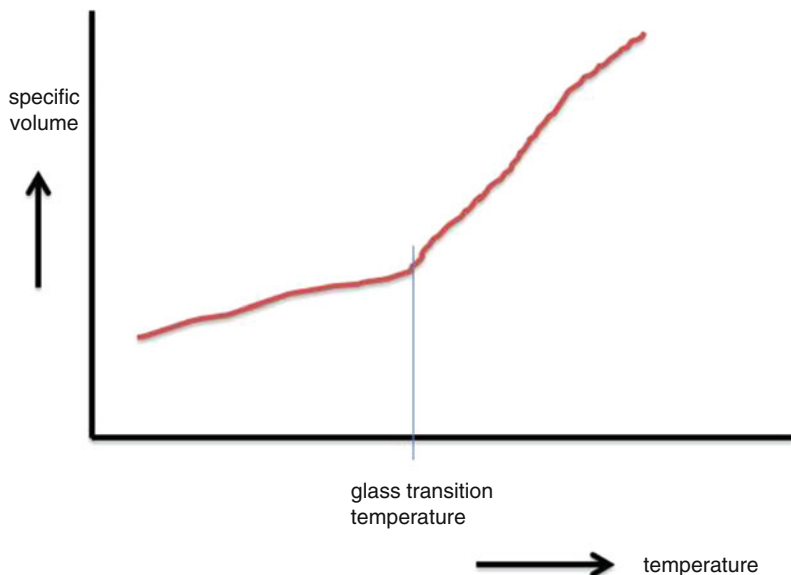
An extent of this (segmental) chain motion and free volume influences a lot of the polymer properties, e.g., a transport of the different low-molecular-weight media through the membranes made of these polymers (Strathmann 2011). For example, a nonporous (dense) membrane made of a rubbery polysiloxane [$-\text{Si}(\text{R})_2-\text{O}-$] $_n$, where R is often CH_3] shows a much higher gas permeation (and also diffusivity) in comparison with those made of common glassy polymers at room temperature (Pandey 2001; Bernardo et al. 2009). But their selectivity is traditionally low (Robeson 2008).

Some polymers (e.g., polyethylene, polyamides) include both amorphous and crystalline fractions, and they are called semicrystalline ones. Chains of such polymers may be organized in spherulites having a well-ordered lamellar structure (i.e., a folded chain) with an incorporated disordered amorphous fraction (Fig. 3).

Amorphous polymers are usually transparent; semicrystalline ones are opaque. A segmental mobility of the amorphous regions in semicrystalline polymers varies from that of the amorphous polymer. These regions are affected by the presence of crystalline phase, and this phenomenon influences also transport characteristics of the

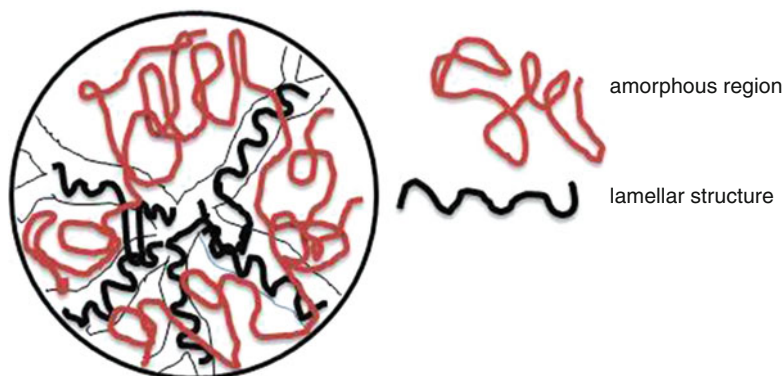
Amorphous Polymers and the Amorphous Region,

Fig. 2 Temperature dependence of the specific volume of an amorphous polymer



Amorphous Polymers and the Amorphous Region,

Fig. 3 Schematic arrangement of the spherulite



penetrating media. Traditionally, the “more dense” crystalline phase decreases a chain mobility and prolongs a transport trajectory of penetrating media, and – as a consequence of this – their permeability decreases (Pandey 2001). Nevertheless, some exceptions were also found, e.g., an increase of gas permeability in a polylactide membrane with its increasing crystallinity (Colomines et al. 2010).

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Amphipathic Molecules

► [Amphiphilic Molecules](#)

Amphiphiles

- [Amphiphilic Molecules](#)

Amphiphilic Block Copolymers

- [Amphiphilic Molecules](#)

Amphiphilic Conetwork Membrane

- [Amphiphilic Membrane](#)

Amphiphilic Film

- [Amphiphilic Membrane](#)

Amphiphilic Lamellar Structure

- [Amphiphilic Membrane](#)

Amphiphilic Membrane

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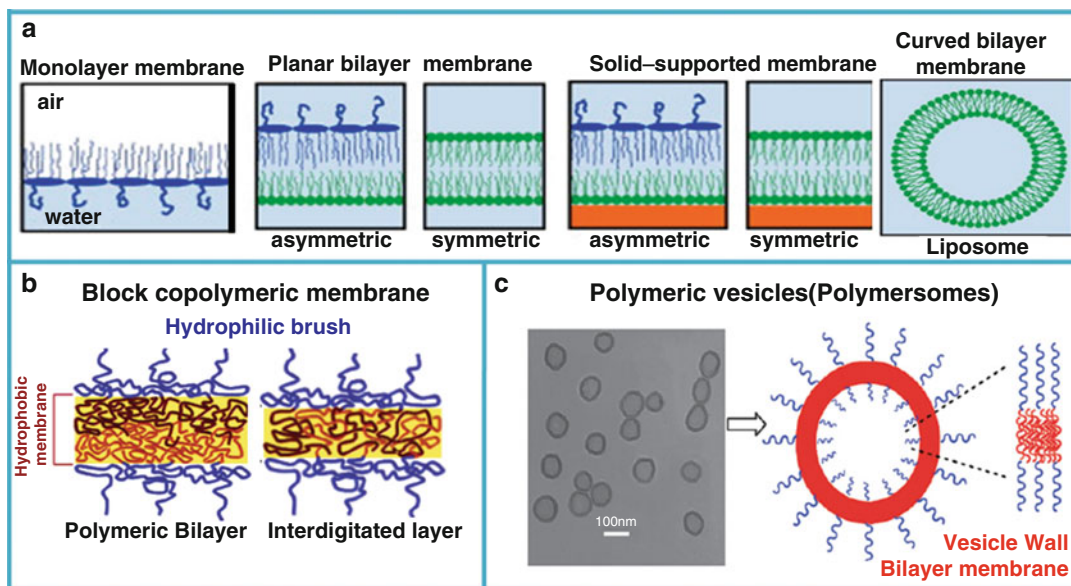
Synonyms

[Amphiphilic conetwork membrane](#); [Amphiphilic film](#); [Amphiphilic lamellar structure](#); [Amphiphilic monolayer/bilayer](#); [Hydrophilic-hydrophobic membrane](#); [Lipid monolayer/bilayer](#); [Two-dimensional amphiphilic aggregates](#)

Amphiphilic Membrane from Amphiphilic Molecules

Amphiphilic membrane is a kind of planar arrays of one or two monomolecular layers, which are derived from self-assembly of amphiphilic molecules, such as lipids, surfactants, or block copolymer amphiphiles, through noncovalent interactions in aqueous solution or in oil–water mixtures (Lipowsky et al. 1992; Lipowsky 1991). Amphiphilic molecules, such as lipids or surfactants, possess a hydrophilic (lipophobic) head and a hydrophobic (lipophilic) tail consisted of one or two hydrocarbon chains. The hydrophilic head prefers to be in contact with water in aqueous solution, whereas the hydrophobic tail tends to minimize contact with water. In aqueous solution or in oil–water mixtures, such molecules can form a variety of structures (assemblies) due to the hydrophobic effect. In many cases, the molecules form amphiphilic membranes consisted of a monomolecular monolayer of amphiphiles. For example, the phospholipid molecules self-assemble vertically as a monolayer film at the interface between water and air, with their hydrophilic head groups immersed in the water and their hydrophobic tails pointed to the air, as shown in Fig. 1a (Costa et al. 2012). The two-dimensional membrane also can be observed in the lamellar aggregates of surfactant molecules at the oil–water interface in a microemulsion. These two-dimensional monomolecular insoluble membranes formed by spreading amphiphilic molecules on the surface of a liquid are also referred to as Langmuir monolayers (Kaganer et al. 1999; Dücks and Schmid 2001). These one-molecule-thick films display many advantages compared to the other model membranes, which are excellent model systems for studying chemical and biological reactions in two dimensions, dynamic adsorptions and interfacial behaviors, as well as membrane hydrolysis processes (Dynarowicz-Łatka et al. 2001). These monolayers also provide a way to manipulate molecules and construct artificial materials for optical, electronic, or sensor applications (Kaganer et al. 1999).

Amphiphilic molecules dissolved in water at appropriate concentrations can also self-assemble into bilayer structures with a thickness of only a



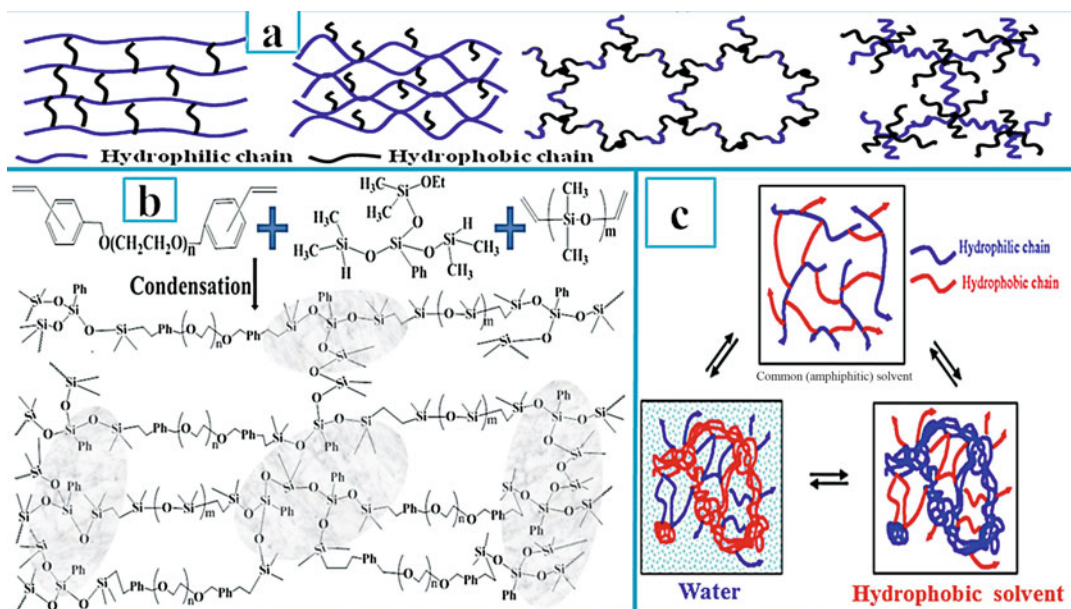
Amphiphilic Membrane, Fig. 1 Typical amphiphilic membranes based on the self-assembly of amphiphiles. (a) Phospholipid molecules. (b) Amphiphilic diblock copolymers. (c) Amphiphilic diblock copolymers. The

schematic illustrations were made according to the references (Gutsmann and Seydel 2010; Battaglia and Ryan 2005; Du and O'Reilly 2009 with permission from Elsevier and The Royal Society of Chemistry)

few nanometers, as shown in Fig. 1a. Such bilayer membranes consist of two opposing layers of amphiphiles. The hydrophilic heads are oriented towards the surrounding water, while the hydrophobic tails overlapped and packed the middle of the membrane (Lipowsky et al. 1992; Lipowsky 1991). The bilayer membranes are usually found either in the form of closed vesicles or as part of a multilayer stack of lamellae (Chowdhury and Stauffer 1991; Leibler and Andelman 1987). Particularly, lipid bilayers are one of most important amphiphilic membranes due to their properties and their importance in biological systems. The lipid bilayers are a general structure of cell membrane of almost all living organisms, forming the barrier between cytosol and extracellular environment. Many biological functions and cellular processes for cell-surface recognition, signaling, and transport are performed at such biological interfaces (Shillcock and Lipowsky 2002; Han et al. 2013). The importance of the lipid bilayers have aroused great interest in fabricating artificial bilayer membranes, including both freestanding lipid membranes and solid-supported membranes. These bilayer membranes are popular models of cell membranes, which

have universal application in biology and nanotechnology, such as ion channel activity, lipid phase separation, charged lipids manipulation, cell signaling, cell-cell interaction, membrane base biosensor, and protein binding (Han et al. 2013).

Amphiphilic membranes prepared from the self-assembly of lipids have a certain amount of fluidity, depending crucially on the temperature as well as chain structures and physicochemical properties of amphiphiles. Therefore, their permeability, stability, and mechanical characteristics are not particularly well controlled (Illya et al. 2005; Discher et al. 1999; Discher and Eisenberg 2002). Like natural phospholipids, amphiphilic block copolymers in water can also self-assemble into various ordered lamellar structures. The morphology of the resultant nanostructures was controlled by many factors. The volume ratio of the hydrophilic to hydrophobic block of membrane-forming amphiphiles was proposed to be one of the most important parameters in the self-assembly process. Bilayer membranes, as shown in Fig. 1b, can be formed if the hydrophilic/hydrophobic length ratio is sufficiently small (i.e., the critical aggregation



Amphiphilic Membrane, Fig. 2 Amphiphilic membranes based on amphiphilic polymer conetworks. (a) Typical structures of segmented amphiphilic polymer conetworks. (b) A typical synthesis method of amphiphilic polymer conetworks. (c) Amphiphilic membranes

concentrations approach zero) (Battaglia and Ryan 2005; Du and O'Reilly 2009). Moreover, the lamellar structures of amphiphilic diblock copolymers are often thermodynamically unstable, which tend to close to form a hollow structure, i.e., polymer vesicles or polymersomes (Fig. 1c). Compared to lipid-based vesicles, the stiffness and stability of polymersomes are higher because of the length and conformational freedom of polymer chains, which made polymersomes have potential for more applications in materials science, biology, and biomedical science (Battaglia and Ryan 2005; Du and O'Reilly 2009).

Amphiphilic Membrane Based on Amphiphilic Conetworks

The term “amphiphilic membrane” also refers to a polymeric membrane based on amphiphilic conetworks (Fig. 2a), which consist of hydrophilic and hydrophobic chain segments covalently bonded to each other. The cocontinuous interconnected hydrophilic/hydrophobic phases

response to hydrophobic and hydrophilic solvents. The schematic illustrations were made according to the references (Patrickios and Georgiou 2003; Erdodi and Kennedy 2006 with permission from Elsevier)

make amphiphilic conetworks exhibit amphiphilic characters (Isayeva and Kennedy 2004; Bruns et al. 2005; Erdodi and Kennedy 2006). They commonly can be synthesized by a multistep condensation (Fig. 2b) or a free-radical copolymerization with simultaneous cross-linking (Erdodi and Kennedy 2006; Patrickios and Georgiou 2003). As shown in Fig. 2c, such networks can swell in both aqueous and organic media without losing their dimensional stability and without encountering macroscopic phase separation or polymer leaching, which have a great potential for applications such as contact lenses, pervaporation membranes, and drug delivery systems (Erdodi and Kennedy 2006; Patrickios and Georgiou 2003; Isayeva and Kennedy 2004).

Cross-References

- [Amphiphilic Molecules](#)
- [Cell Membrane](#)
- [Langmuir and Langmuir–Blodgett \(LB\) Films](#)
- [Plasma Membrane](#)

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Amphiphilic Molecules

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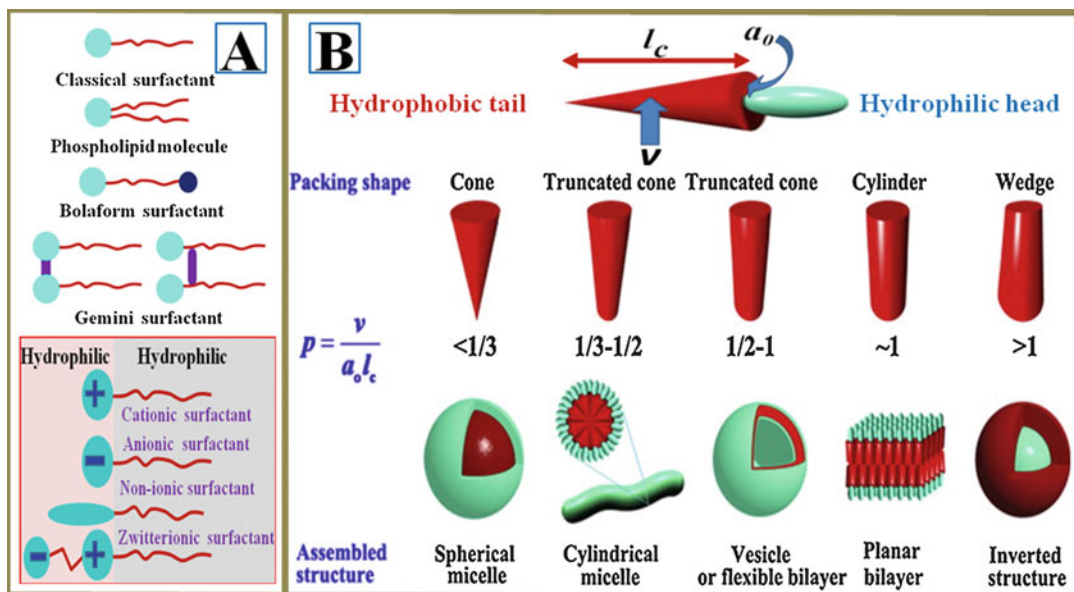
Synonyms

Amphipathic molecules; Amphiphiles; Amphiphilic block copolymers; Amphiphilic polymers; Amphipols; Detergents; Emulsifiers; Hydrotropes; Lipids/phospholipids; Soaps; Surfactants

Amphiphilic molecules is a general term that describes any compound that contains two distinct covalently bonded components with different affinity for the solvent in the same molecule, in which one part possesses a high affinity for polar solvents (such as water), and another part has a strong affinity for nonpolar solvents, such as hydrocarbons, ethers, and esters. Surfactants, polymer amphiphiles, and some lipid molecules, containing both hydrophilic and hydrophobic components, are typical examples of amphiphilic molecules.

Low Molecular Weight Amphiphiles

Surfactants (surface active agents), more popularly known as soaps, are among the oldest known chemicals used by human. This type of molecules now play a crucial role in many areas

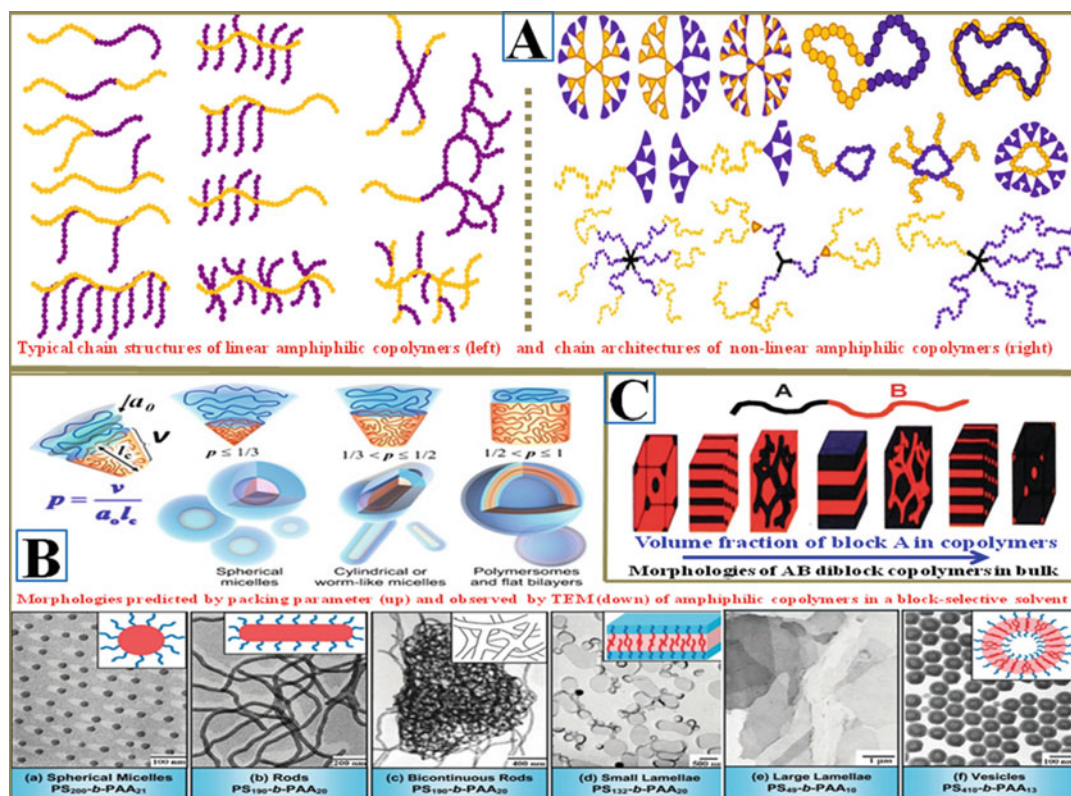


Amphiphilic Molecules, Fig. 1 Schematic illustrations of surfactants and corresponding assemblies. (a) Structures of surfactants, (b) Surfactant assemblies and the effect of the packing parameter (p). $p = v/(a_0 l_c)$, determining the assemblies' morphologies, where v is the volume of the hydrophobic segment, a_0 is the contact area of the polar head group, and l_c is the length of the hydrophobic

segment. When $p < 1/3$, spheres are formed; when $1/3 < p < 1/2$, cylinders will be favored; when $1/2 < p < 1$, flexible lamellae or vesicles are produced; finally, when $p = 1$, planar lamellae are obtained. If $p > 1$, reversed structures can be observed (The schematic illustrations were made according to the Zhang et al. (2012) with permission from Elsevier)

such as cleaning products, food, cosmetics, pharmaceuticals, and oilfield chemicals as well as biological processes (Holmberg et al. 2002; Schramm et al. 2003; Chevalier 2002). Generally speaking, surfactants possess a hydrophilic head which might be either charged or uncharged and a hydrophobic tail composed of one or more hydrocarbon, fluorocarbon, or dimethylsiloxane chains (Fig. 1a). According to the nature of their polar head group, these molecules can be typically classified into four categories (Fig. 1a): (1) cationic surfactants containing a positively charged head group (e.g., fatty amine salts and quaternary ammoniums); (2) anionic surfactants with a negatively charged head group such as carboxylate, sulfate, sulfonate, or phosphate; (3) nonionic surfactants with an oligo(ethylene glycol) chain as hydrophile; and (4) Zwitterionic surfactants comprised of a long hydrocarbon chain and a hydrophile containing both positive and negative charges. Some new surfactants such as bolaamphiphiles and Gemini surfactants have

attracted much attention because of greater surface activity (Chevalier 2002; Fuhrhop and Wang 2004). Owing to their special structures and amphiphilic properties, surfactants can reduce the surface tension when adsorbing at air–water or oil–water interface at very low concentration, which can offer a number of surface chemistry functions, such as solubilizing, wetting, emulsifying, foaming, and surface conditioning (Holmberg et al. 2002; Schramm et al. 2003). More importantly, these amphiphilic molecules can spontaneously segregate and self-assemble into a wide variety of nanostructures through solvophobic interactions, when the concentration of amphiphiles is above a certain critical concentration (i.e., the critical micelle concentration, CMC, defined as the concentration of surfactants above which micelles are spontaneously formed) (Holmberg et al. 2002). The morphologies, including spherical micelles, cylindrical micelles, lamellae, vesicles, etc. (Fig. 1b), are governed by the molecular structure of the surfactants as well



Amphiphilic Molecules, Fig. 2 Schematic illustrations of typical chain structures (a) and morphologies of amphiphilic polymers in solution (b) and in bulk (c) (The

schematic illustrations were made according to the Wang and Grayson (2012), Mai and Eisenberg (2012) with permission from Elsevier and The Royal Society of Chemistry)

as by physical parameters such as concentration, temperature, and ionic strength. The size and shape of the aggregates were often predicted by using the packing parameter (p), which is the ratio of area occupied by the hydrophilic head and hydrophobic groups of amphiphiles (Israelachvili et al. 1976). The properties and performances of surfactants are closely related to their self-assembly behaviors, and thus it still requires much deeper understanding on the relationship among the molecular structures, aggregation behaviors, and application properties of these amphiphiles.

Macromolecular Amphiphiles

Amphiphilic polymers are another kind of typical amphiphilic molecules of high molecular weight

(Holmberg et al. 2002; Nagarajan 2011). Due to the coexistence of both hydrophobic and hydrophilic moieties on the same molecule, they are also able to self-assemble into a number of nanostructures in solution (Fig. 2b) and in bulk (Fig. 2c), which are analogous to those aggregates of the small-molecule amphiphiles. Moreover, their self-assembly behaviors follow the same principle as that of surfactants (Mai and Eisenberg 2012), and thus at least to some degree, the morphologies of polymer assemblies can also be predicted by the dimensionless p , as shown in Fig. 2b. In addition, the hydrophilic/hydrophobic ratio, copolymer concentration, solvent properties, etc. can significantly affect the morphologies of the final nanostructures (Mai and Eisenberg 2012). Due to the great versatility of polymers in terms of their molecular weight, chain architecture, polydispersity, and reactivity as well as

synthetic diversity, amphiphilic polymers can provide greater opportunities for flexibility, diversity, and functionality. This is especially true in the light of recent advances in controlled/living radical polymerization chemistry, such as ATRP and RAFT polymerization, for the preparation of polymers of various architectures, including linear block copolymers, graft copolymers, dendritic polymers, star-like polymers, and cyclic polymers, as shown in Fig. 2a. Under certain conditions, all of these types of amphiphilic polymers can also self-organize into aggregates of diverse morphologies (Mai and Eisenberg 2012; Wang and Grayson 2012). In addition, the size, morphology, and function of the resulting polymeric assemblies can be easily controlled by adjusting the structure of the amphiphilic copolymers. Compared to small-molecule aggregates, polymer aggregates exhibit higher stability and durability (Mai and Eisenberg 2012). Particularly, stimuli-sensitive polymer assemblies that can respond to subtle changes in surrounding environment such as pH, temperature, and solvent quality can be feasibly realized via the self-assembly of polymer amphiphiles with responsive groups (Schacher et al. 2012; Zhang et al. 2012). Therefore, it is no wonder that amphiphilic polymers and their assemblies have attracted considerable attention and achieved significant success in many fields, such as biomedicine, biomaterials, pharmaceuticals, microelectronics, and photoelectric materials.

Cross-References

- [Lipid Monolayer/Bilayer](#)
- [Surface Tension](#)

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Amphiphilic Monolayer/Bilayer

- [Amphiphilic Membrane](#)

Amphiphilic Polymers

- [Amphiphilic Molecules](#)

Amphiphilic Substances: Amphiphiles

- [Encapsulation](#)

Amphipols

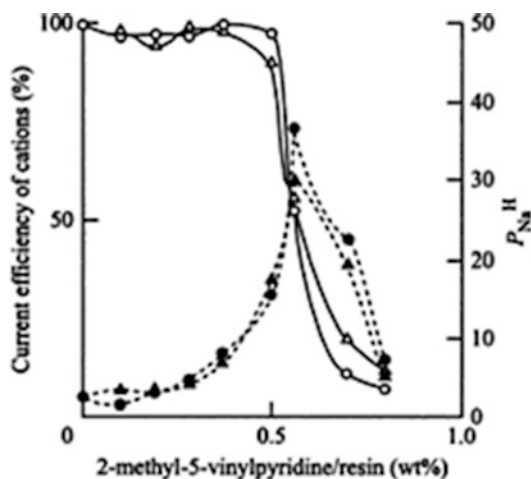
- [Amphiphilic Molecules](#)

Amphoteric Ion Exchange Membrane

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Amphoteric ion exchange membrane is a kind of membrane containing random arrangements of both cation and anion exchange groups. When firstly proposed by Söllner in 1932 (Söllner 1932), amphoteric ion exchange membranes mainly refer to membranes having a combination of weak acidic (cation exchange) and weak basic (anion exchange) groups. Nowadays, they are expanded to include membranes containing a combination of weak acidic (or weak basic) with strong basic (or acidic) functionalities or a combination of strong acidic and basic groups. Basically, there are four types (Sata 2004): (1) membranes in which both anion and cation exchange groups are distributed at random during the preparation procedures, such as copolymerization, (2) snake cage-type amphoteric membranes, (3) polysalt membranes, and (4) membranes prepared by a “layer-by-layer” method. The amphoteric ion exchange membranes can show superior antifouling properties, peculiar selectivity, and permeability and hence are useful in the biomedical and industrial fields, such as medical devices (e.g., hemodialysis membrane), separation of ionic drugs and proteins, and depletion of electrolytes by nanofiltration or piezodialysis as well as high performance gel actuator. Membrane having properly combined anion and cation exchange groups shows selective permeability for inorganic salts and, therefore, is able to separate a low molecular organic substance from an inorganic salt, acid, or alkali as well as salt from acid or salt from alkali (Eguchi et al. 1981).



Amphoteric Ion Exchange Membrane, Fig. 1 Transport number of hydrogen ions relative to sodium ions (P_{Na}^H) and current efficiency of cations to the composition of amphoteric ion exchange membranes. (O, ●): quaternized membranes (N-methyl pyridinium and sulfonic acid groups); (Δ, ▲): tertiary amino groups membrane; (pyridinium hydrochloride and sulfonic acid groups); (●, ▲): P_{Na}^H ; (O, Δ): current efficiency (%). Electrodialysis was carried out at a current density of 20 mA cm^{-2} using a mixed solution of 0.25 N sodium chloride and 0.25 N hydrochloric acid for 60 min at 25.0°C (Yamane et al. 1965)

Meanwhile, some of the membranes have compositions that show hydrogen ion permselectivity relative to sodium ions in electrodialysis (Yamane et al. 1965) (Fig. 1).

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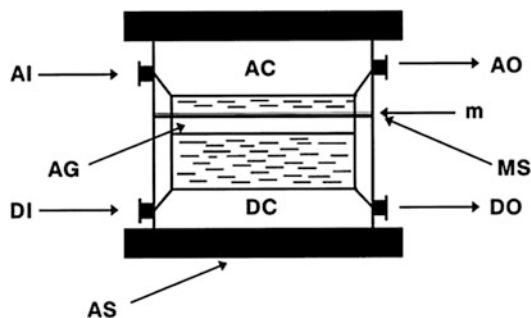
Analytical Pervaporation

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The relatively new developed pervaporation in analytical chemistry is in principle a separation technique for the removal of volatile analytes or their volatile derivatives from the sample matrix. Also, it can be used for sample pretreatment, e.g., for solid samples where leaching and derivatization of the analytes are done simultaneously. Analytical pervaporation can be defined as the integration of evaporation and gas diffusion in a single module. Through a porous membrane, the volatile substances present in a heated donor phase evaporate. And on the other side of the membrane, the vapor condenses on the surface of a cool acceptor stream. The driving force for the separation is due to the temperature difference, which leads to a vapor pressure difference across the membrane. For analytical pervaporation, an important feature is that the existence of a constant-volume air gap between the sample in the donor chamber and the membrane, which hinders any contact between them. As a result, the clogging and/or deterioration of the membrane can be avoided (Luque de Castro 1998).

The conventional version of the analytical pervaporation module is shown in Fig. 1 and consists of the following parts: (i) a lower donor chamber (DC) in which the sample containing the analyte is introduced, either by injection or by continuous aspiration for liquid samples and by direct weighing for solid samples, (ii) an upper acceptor chamber (AC) in which an appropriate fluid is circulated for receiving the pervaporated analytes, (iii) a membrane support (MS) approximately 1 mm thick, and (iv) spacers of varying thickness (between 2 and 10 mm) which can be placed above or below the membrane support in



Analytical Pervaporation, Fig. 1 Conventional pervaporation module. DC donor chamber, AC acceptor chamber, MS membrane support, *m* membrane, AG air gap, AS aluminum supports, DI, DO inlet/outlet of donor stream, respectively, AI, AO inlet/outlet of acceptor stream, respectively

order to increase the volume of the corresponding chamber. The different parts of the module are aligned by inserting metallic rods into four orifices and a closer contact is achieved by screwing them between two aluminum supports (AS). The whole module is normally made of methacrylate, which permits continuous monitoring of the sample level in the lower chamber during the experiments Luque de Castro and Papaefstathiou (1998).

Constantly being hydrophobic, the membranes for analytical pervaporation are usually employed in ultrafiltration and gas-diffusion processes. Practically, polytetrafluoroethylene (PTFE) is the most frequently used membrane material, followed by hydrophobic polyvinylidene fluoride (PVDF) Luque de Castro and Gdmiz-Gracia (2000). In combination with the large surface area of both the donor and acceptor chambers, the ultrafiltration membranes, which are very thin, lead to their easy bending. In result, the flux of the permeating component changes through an altered membrane area, and therefore, it leads to a change in the efficiency of the process in addition to reproducibility problems; consequently, the membranes must be changed quite often. Due to their thickness, gas-diffusion membranes are not so easily bent, so the same membrane can be used

over longer periods. The efficiency of the process is influenced by the pore size of the membrane (or its directly proportional thickness) and hence the sensitivity of the method; it affords application to samples with variable analyte concentrations, as a result.

Analytical pervaporation can be used for the determination of a single analyte or a number of analytes, being of inorganic, organic, or organo-metallic nature. Application of analytical pervaporation in the environmental field has been reported especially for food analysis Amador and Luque de Castro (2000). which is the analytical field in which pervaporation has been most widely applied. Other fields of application of pervaporation have been pharmaceutical and clinical analyses.

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Anion-Exchange Membrane (AEM)

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The **anion-exchange membrane (AEM)** is a thin film with anion-exchange groups (positively charged groups) and permeates anions selectively. AEMs are classified according to the species of the ion-exchange groups and materials constituting the membrane and microstructure.

Anion-exchange groups are positively charged groups: primary, secondary, and tertiary amino groups, quaternary ammonium groups, tertiary sulfonium groups, quaternary phosphonium groups, cobalticinium groups, and other groups that provide a positive fixed charge in aqueous or mixed water and organic solvent solutions. Based on the materials constituting membranes, AEMs can be classified as (i) organic membranes, (ii) inorganic membranes, and (iii) composite membranes of inorganic ion exchangers and organic polymers. AEMs are also classified into two types by their microstructure: heterogeneous and homogeneous. Heterogeneous AEMs consist of finely powdered anion exchanger and an inert binder polymer. Various methods have been reported for preparing homogeneous AEMs. A typical example of a hydrocarbon AEMs is a copolymer membrane composed of styrene and divinylbenzene with benzyltrimethylammonium groups. These membranes will be prepared, for example, by the reaction of trimethylamine with a copolymer membrane prepared from chloromethylstyrene and divinylbenzene or by alkylation with alkyl halide of a copolymer membrane prepared from vinylpyridine and divinylbenzene.

Though AEMs have been used in many fields, most are used in electrodialysis, separation of electrolysis, and solid polymer electrolytes for fuel cells. The properties required depend on the intended application of AEMs. Generally required properties are (1) low electrical resistance, (2) high transport number of anions, (3) low diffusion coefficient of electrolytes, (4) low osmotic water and low electroosmotic water, (5) antifouling properties, (6) mechanical strength, (7) dimensional stability, (8) high chemical stability and durability, and (9) low cost (Sata 2004).

AEMs with low sulfate ion permeability have been industrially used to prevent precipitation of calcium sulfate in the AEMs and electrodialyzer. A nitrate ion permselective AEM has been developed and has contributed to human health because the concentrations of nitrate ions are greatly increased in groundwater. To prepare these

functionalized AEMs, ordinary AEMs are modified by suitable chemical or physical methods. For example, most commercially available homogeneous AEMs are mainly cross-linked with divinylbenzene. When the contents of divinylbenzene increase or compact layers are formed on the AEMs, the pore size of the membrane decreases and the transport number of sulfate ions, which are bulky relative to chloride ions, decreases.

Fouling of separation membranes is a common problem. AEMs are fouled by ionic materials of medium molecular weight such as ionic surfactants having the charge opposite to the fixed charged of the membrane. Almost all of organic foulants in many effluent streams have negative charges; hence, fouling of AEMs due to deposition and/or adsorption of the foulants on/in the AEM is one of the serious problems in their applications. The pore size of the AEM is generally recognized to be about 1 nm; therefore, ions of medium molecular weight permeate with difficulty through the membrane. Consequently, the fouling can lead to an unacceptably high stack resistance and replacement of membranes in an electrodialysis system due to clogging of the membrane pores with the medium molecular weight ions. To alleviate the problem of organic fouling, there are basically two methods on the membrane side: first, to increase the pore size of the membrane to allow easy permeation of large ionic materials and, second, to prevent penetration of the materials into the membrane at the membrane surfaces. There are two methods to prevent penetration of large organic materials into the membrane matrix: forming a thin charged layer opposite in sign to the ion-exchange groups of the membrane or forming a very thin and dense layer on the membrane surfaces.

Reference

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Anion-Exchange Resin

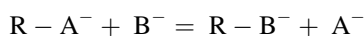
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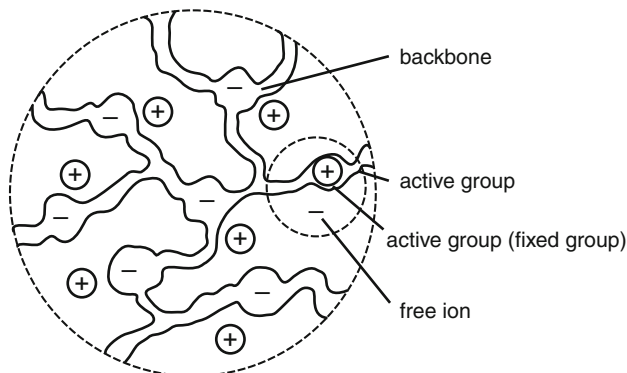
Anion-exchange resin contains positively charged groups, such as $-\text{NH}_3^+$, $-\text{NRH}_2^+$, $-\text{NR}_2\text{H}^+$, $-\text{NR}_3^+$, $-\text{PR}_3^+$, $-\text{SR}_2^+$, etc., which are fixed to the membrane backbone and allow the exchange of anions but repulse cations. As shown in Fig. 1, the active groups existed in the body of resin determine its chemical behavior. It has a highly developed structure of pores on the surface, which could easily trap and release ions.

There are two main types of anion-exchange resins differing in their active groups: strongly basic and weakly basic. (1) Strongly basic resins are highly ionized, and their chemical behavior is similar to that of a strong base which can be used over the entire pH range. They can react with anions in solution and convert an acid solution to pure water. The exhausted resin can be regenerated with concentrated sodium hydroxide (NaOH) and converted to the hydroxide form. (2) The degree of ionization of weakly basic resin is strongly influenced by pH because it is like a weak base. The weak base resin does not have a hydroxide ion form as does the strong base resin. Consequently, its regeneration needs only to neutralize the absorbed acid and does not need to provide hydroxide ions. Less expensive weakly basic reagents such as ammonia (NH_3) or sodium carbonate can be employed.

The selectivity of a resin for a given ion is measured by the selectivity coefficient (K), as for the reaction



The K can be expressed as $K = (\text{concentration of } \text{B}^- \text{ in resin} / \text{concentration of } \text{A}^- \text{ in resin}) \times$

Anion-Exchange Resin,**Fig. 1** Diagram of anion-exchange resin

(concentration of A^- in solution/concentration of B^- in solution).

In general, introducing ionic groups could start with a monomer containing a moiety, a polymer film, or start with polymers or polymer blends (Helfferich 1962; Strathmann 2004). As summarized in our recent book chapter, the specific implementation methods include (1) amidoalkylation of cross-linking polystyrene, (2) copolymerization of (chloromethyl) styrene, (3) chloroacetylation of polymers, (4) acetylation of cross-linked polystyrene, and (5) grafting vinylbenzyl ammonium chloride onto inert polymers (Xu 2009).

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Annealing of Polymer Membranes

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Annealing can be defined as a process where a material undergoes a heat treatment to a certain temperature, is kept there for a definite time, and is

then cooled to room temperature in order to alter the material properties. The annealing process is time and temperature dependent.

Annealing of polymers is a heating of a polymeric part to below its glass transition temperature in order to relieve the internal stresses introduced during its fabrication (molding, cooling after molding, machining, welding, etc.).

Annealing of conjugated polymers and polymer blend films is a widely used process that achieves optimal film morphology and therefore improves material properties, such as electrical mobility for photovoltaic devices and other applications. Annealing of ion-conducting polymers reduces the excessive swelling observed in presence of water.

In particular, annealing is used (Young and Lovell 1991):

- To increase the melting point of some polymers because it facilitates the melting of small and irregular crystals in favor of larger and better formed ones
- To reduce or cancel deformations previously provoked at higher temperature which remain as frozen (permanent) deformations when the material is cooled to room temperature
- To increase crystallization
- To decrease the free volume between polymeric chains thus inducing a mechanical stabilization of polymeric materials

Annealing of liquid crystalline polymers between the glass transition temperature and the

melting temperature leads to an increased level of crystallinity and increased crystalline perfection analogous to the behavior of conventional semicrystalline polymers. Annealing at or above the melting point also leads to enhanced crystallinity and crystalline perfection.

The annealing of semicrystalline polymers may change the crystal structure, the degree of crystallinity, the perfection of the crystals, the orientation of both crystalline and amorphous phases, their contiguous structural morphology, and the number of tie chains between the crystallites. Morphological changes are also observed on annealing bulk-crystallized samples. Polymorphism may result due to annealing crystalline polymers as its one crystalline form transforms into another. The concept that mechanical stabilization was due to a generic decrease of the free volume between ionomer chains when thermally treated was abandoned and replaced by the consideration that the mechanical stabilization was induced by an increased crystallization of a preexisting semicrystalline phase (Alberti et al. 2013).

Thermal annealing is a simple route for stabilizing glassy polymers via the densification of their polymer chains and is accomplished through thermal treatment of the glassy thermoplastics. For amorphous polymers, the thermal treatment can play a very important role in changing the morphology. If the temperature is lower than the glass transition temperature T_g , the polymer chains are mainly immobile, thereby maintaining the existing morphology; however, if the annealing temperature is greater than the T_g , the polymer chains will relax. It has been found that the morphology can be modified upon annealing at a temperature higher than the T_g , thus changing the physical properties of the polymers.

A certain amount of molecular rearrangement must take place during crystallization but this rearrangement cannot arise through large-scale molecular diffusion as the process is occurring in the solid state. Thermal treatments were believed to be more and more efficient as the temperature increases and therefore empirical short treatments were performed at high temperatures. Thus, the annealing temperature (T_{ann}) was connected with

the crystallization temperature (T_c) and it became clear that the annealing temperature cannot be higher than the melting temperature (T_m) of the semicrystalline phase.

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Antibiological Fouling Surface

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Antibiological fouling surface is a surface having the property to resist the attachment or proliferation of living organisms. In membrane systems, the main organisms of concern for biological fouling are microorganisms. Antibiological fouling membranes may resist biological fouling, or biofouling, by three main mechanisms: reducing the attachment of microorganisms to the surface, killing the microorganisms to prevent their multiplication, or inhibiting their proliferation on the membrane surface (De Kwaadsteniet et al. 2011).

Biological fouling can be reduced by reducing the adhesion of microorganisms and biological foulants to the membrane. Adhesion of foulants on a membrane depends on the physicochemical properties of the surface and is increased with higher surface roughness, hydrophobicity, and electrostatic charge. Surface roughness increases fouling by increasing the contact area between the cell and the surface (Vrijenhoek et al. 2001). Strategies to reduce the surface roughness include changes in the fabrication procedure or filling

the valleys of the surface with polymers or nanomaterials (Rana and Matsuura 2010). Hydrophobic surfaces increase fouling due to the hydrophobic nature of most biological foulants. Increase in the hydrophilicity of a surface generates a hydrated layer that reduces the adhesion of hydrophobic proteins and microorganisms. To achieve a more hydrophilic surface, the membrane may be coated or functionalized with hydrophilic polymers and nanomaterials or chemically modified by treating the membrane with plasma, UV light, different acids or bases, and oxidizing agents (Rana and Matsuura 2010). Electrostatic interactions may increase the adhesion of microorganisms on the membrane. Proteins and microbial cells are generally negatively charged in natural pH. Therefore, lowering the surface charge may decrease foulant adhesion by increasing the electrostatic repulsion. The surface charge of a membrane can be modified by changing the nature of the functional groups present on the membrane surface (Rana and Matsuura 2010). Finally, adhesion of biological foulants and microorganisms may be decreased by surface modification with polymer brushes. The use of long-chain molecules such as polyethylene glycol increases steric repulsion between foulants and the membrane surface (Banerjee et al. 2011). The antifouling effectiveness of the polymer brushes depends on the length and density of the polymer layer.

Biological fouling can be reduced by inactivating microorganisms in order to prevent their development on the membrane surface. Antimicrobial compounds can be integrated in a membrane by including them in the polymer solution during membrane fabrication or by post-fabrication membrane functionalization. These antimicrobial compounds may be biocide-releasing materials, contact-action antimicrobial agents, or photocatalytic materials (Banerjee et al. 2011).

Biological fouling may be reduced by preventing the development of microbial communities without directly killing the microorganisms. This is accomplished by using bacteriostatic or quorum-sensing inhibitors that prevent the assembly of deposited microorganisms into a biofilm.

Such compounds can be directly attached to the membrane or included in a slow-release platform such as polymeric particle (Glinel et al. 2012).

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Antibiotic Production by Membrane Operations

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Synonyms

Membranes in antibiotic production

Antibiotics are medicines produced by fermentation that fight bacterial infections; they can either kill other microorganisms or inhibit their growth.

The development of antibiotics started with the discovery of penicillin by Fleming in 1928 that gave rise to many other discoveries in the subsequent 40 years. The number of new antibiotics on the market had a steady increase until the 1980s, but the unrestrained use of antibiotics led to the emergence of antibiotic-resistant pathogens and the number of approved antibiotics decreased constantly in the last 30 years (Coates

et al. 2011). The research for therapeutics endowed with a broaden antimicrobial range brought to the development of semisynthetic antibiotics which are produced by chemical or enzymatic transformation of penicillin and cephalosporins (Srirangan et al. 2013). Penicillin is still one of the antibiotics with the largest annual bulk production; it is part of the β -lactam antibiotic class, with about 15 billion US\$ annual sales and a market share of about 65 % of the total world antibiotic market (Elander 2003).

The production of antibiotics typically involves a series of process steps consisting of fermentation, removal of biomass, purification, and crystallization (Koltuniewicz 2010). Membrane operations can be integrated within this process sequence, both in the upstream and in the downstream processing, for production of either natural or semisynthetic antibiotics.

In upstream processing, membranes are utilized for ancillary operations and, in particular, for sterile filtration of culture media and air which is supplied as a source of oxygen for aerobic fermentation, whereas in the downstream part of the process, they can be utilized as alternative unit operations. In the downstream section, membranes can be applied for cell harvest, clarification, and concentration. Among the membrane technologies used for recovery and purification, crossflow microfiltration and ultrafiltration can be employed for biomass separation, often in combination with diafiltration to improve product yield and purity (Lipnizki 2010).

Antibiotic recovery from fermentation broths can be done directly if the product is extracellular, as in penicillin production, or following cell disruption if the product is intracellular, as for some tetracyclines. Since antibiotics are relatively small molecules, with molecular weights of less than 2,000 amu, the MF/UF membrane retains the biomass or the cell debris when the antibiotic is an intracellular products, while the antibiotics are found in the permeate side. The clarified antibiotic stream can then be concentrated with nanofiltration and/or reverse osmosis (Lipnizki 2010). Purification of antibiotics is generally carried out with solvent extraction, but depending on the target molecule, absorption or precipitation

may also be used. The introduction of an ultrafiltration step greatly improves the extraction process (Koltuniewicz 2010).

Other membrane technologies like membrane contactors, liquid membranes, and membrane bioreactors are less established; however, they have great potential for industrial applications in antibiotic production.

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Antifouling Membrane Surface

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The term fouling generally refers to an undesirable process in which a surface becomes encrusted due to the undesirable accumulation of foulants, such as biomacromolecules,

microorganisms, hydrocarbons, particles, and colloids from the surrounding environment. Antifouling surface, also referred to as a “stealth surface,” can minimize the intermolecular forces of interactions between the foulants and the synthetic surface so that the foulants can be easily released under low shear stresses. Antifouling surfaces lie at the heart of several contemporary and advanced technologies, ranging from coatings for ship hulls, biomedical implants, biosensors, drug delivery, and membrane separations. Antifouling membrane surface is one kind of antifouling surfaces. The antifouling surface is often relevant to membranes utilized in microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. The major foulants are different for different membrane processes. The main foulants are microorganisms and emulsified oils for microfiltration, biomacromolecules and colloids for ultrafiltration, natural organic matters for nanofiltration, inorganic salts and bioorganic/organic substances for reverse osmosis.

All the strategies for construction of antifouling membrane surface are based on manipulating the physicochemical and/or topography structure of membrane surface to weaken the interactions between foulants and membrane surface and thus inhibiting foulants adsorption or settlement. There are four major types of antifouling membrane surfaces, including hydrophilic surface, hydrophobic surface, amphiphilic surface, and reactive surface. Whitesides (Ostuni et al. 2001) first proposed that antifouling surface showing resistance to protein should have the following four attributes: hydrophilic, hydrogen-bond acceptors but not hydrogen-bond donors, and overall electrically neutral. Poly(ethylene glycol) (PEG)-based polymers and zwitterionic polymers are the most widely used materials to fabricate antifouling membranes. The antifouling mechanism of the PEG-based polymers can be mainly ascribed to the large repulsive hydration forces of tightly bound water layer around the polymer chains via hydrogen bonds or electrostatic attraction. The objective of hydrophilic surface is to prevent the foulants from attaching onto the membrane surface, which is known as “fouling resistance”

(Callow and Callow 2011). The hydrophilic membrane surface can resist the fouling caused by biomacromolecules and natural organic matter. The hydrophobic surface is based on nonpolar, low surface energy hydrophobic polymers, such as poly(dimethylsiloxane) (PDMS) elastomers and fluoropolymers. The mechanism of this hydrophobic surface is that polar molecules (including adhesive protein) barely adhere to membrane surface because of reduced opportunities for forming the hydrogen-bonding and polar interactions. This hydrophobic surface aims to weaken the interfacial bonds so that the attached foulants are more readily removed by hydraulic shear forces, not prevent foulants from attaching, which is known as “fouling release.” The hydrophobic membrane surface is suitable for mitigating the microorganism and hydrocarbon fouling. The amphiphilic surface comprising hydrophilic domains and hydrophobic domains on membrane surface incorporates some of the benefits of both hydrophobic and hydrophilic surfaces. The general aim is to create a dynamic and compositional surface complexity that deters settlement of foulants and reduces the interfacial bonding with membrane surface. The general aim of amphiphilic surface is to combine the nonpolar, low surface energy properties of hydrophobic domains to reduce polar and hydrogen-bonding interactions with foulants, with the well-known protein repellency properties of the hydrophilic domains. The resulting amphiphilic surface may lower the entropic and enthalpic driving forces for the adsorption of the protein and organism. The amphiphilic membrane surface can defer the fouling caused by microorganisms, biomacromolecules, natural organic matter, and hydrocarbons. Therefore, the amphiphilic membrane surface is the most promising antifouling membrane surface for the practical separation system containing a wide range of foulants. The reactive surface immobilizes the component which can degrade organic composition of foulants on membrane surface. The proteases and titania nanoparticles are often immobilized on membrane surface, thus preventing biomacromolecules and microorganism fouling via

enzymatic or photocatalytic degradation (Banerjee et al. 2011).

Several modification approaches are employed to create antifouling membrane surface including surface coating, surface grafting, and surface segregation (Shannon et al. 2008; Rana and Matsuura 2010; Wang et al. 2005). For surface coating, membranes are immersed in a polymer modifier solution or inorganic particles suspension. The modifier is settled on membrane surface to create antifouling coating through van der Waals force or electrostatic interactions. For surface grafting, the modifier is settled on membrane surface via graft polymerization including graft-to and graft-from approach. The termed graft-to approaches consist of the grafting of the pre-synthesized polymer chains with a reactive terminal group. Alternatively, graft-from approaches, in which a polymer is grown in situ from the surface via a surface-adsorbed initiation group, are generally capable of producing denser polymer layers. The surface coating and surface grafting belong to the post-modification approach, whereas surface segregation belongs to the in situ modification approach. The polymer modifiers comprising hydrophobic backbones and hydrophilic side chains are added to casting solution, lining membrane surfaces, and internal pore during the conventional phase inversion process. The hydrophilic chains segregate to membrane surface and endow membrane with surface hydrophilicity and antifouling property, while hydrophobic backbones anchor to membrane matrix polymers to defer loss of modifier during phase inversion process.

The fouling resistance property could be evaluated by flux recovery ratio (*FRR*), while the fouling release property could be evaluated by flux decline ratio (*FDR*). The flux recovery ratio (*FRR*) is the ratio of the water flux after hydraulic cleaning to initial water flux, while the flux decline ratio is the ratio of flux decline (the initial water flux minus the flux for real feed) to initial water flux. The higher the value of *FRR*, the better the fouling resistance property of the membrane; the lower the *FDR*, the better the fouling release property of the membranes.

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Antimicrobial Activity

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Antimicrobial activity of a compound is defined as its capacity to prevent the development of microorganisms. Antimicrobial compounds can be divided into two main categories according to their mechanisms of antimicrobial action: bactericidal and bacteriostatic. Bactericidal agents act by killing bacterial cells. Common bactericidal mechanisms include inhibition of cell wall synthesis, disruption of the cytoplasmic membrane, and inhibition of nucleic acid synthesis. Bacteriostatic agents are compounds that prevent microbial development by inhibiting specific metabolic pathways, thus preventing cell growth and multiplication. Bacteriostatic agents act by inhibiting protein synthesis, by acting on the 30S, 50S, or 70S ribosomal complexes, or by inhibiting other

essential metabolic pathways such as folic acid synthesis. Bacteriostatic effect is reversible and bacteria can proliferate once the bacteriostatic agent is removed (McCarter 2005).

Methods to evaluate the antimicrobial activity can be divided into two categories: diffusion methods and dilution methods. Diffusion methods, also called agar diffusion methods, depend on the diffusion of an antimicrobial compound in an agar plate covered by a bacterial lawn. Antimicrobial activity is measured in terms of the diameter of the zone of inhibition, where bacterial growth is inhibited. The most common agar diffusion assay is the Kirby-Bauer assay. Dilution methods aim to determine the minimum inhibitory concentration of a compound, defined as the minimal concentration that completely inhibits microbial growth, by incubating a defined quantity of bacteria with different dilutions of an antimicrobial compound. Dilution methods can be performed in culture broth or in agar media.

In membrane processes, antimicrobial compounds are used to reduce microbial growth and biological membrane fouling. Antimicrobial compounds can be introduced in the feed effluent continuously or intermittently, during membrane cleaning stages, to kill microorganisms and reduce biofilm development (Matin et al. 2011). Traditional approach using chlorine-based disinfectants is usually effective to control biofilm development; however, chlorine disinfection leads to the formation of undesirable and carcinogenic disinfection by-products. Additionally, chlorine is not compatible with polyamide thin-film composite membranes due to the susceptibility of the aromatic polyamide layer to chlorine attack. Alternative strategies to disinfection of the feed effluent include ozone, UV treatments, or advanced oxidation processes, which produce less disinfection by-products but are limited by their higher cost compared to chlorine. Microbial growth and biofilm development may also be reduced by imparting antimicrobial properties directly to the membrane by modification with antimicrobial compounds. Antimicrobial coating of membranes can be achieved using different types of antimicrobial compounds, such as antimicrobial polymers, antimicrobial peptides,

polycations, silver and metal oxide nanoparticles, carbon nanomaterials, biocide-releasing polymeric structures, and photoactive materials (Banerjee et al. 2011).

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Antimicrobial Membrane

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Antimicrobial membrane (also called antibacterial membrane or anti-biofouling membrane) is a membrane capable of reducing or inhibiting microbial growth on its surface. The biocidal ability of the antimicrobial membrane can generally be exerted by (1) active amphiphilic polymers or synthetic mimics of naturally occurring antibacterial peptides, (2) microbe-repelling anti-adhesive polymers, and (3) composite materials containing various slow-releasing biocides (Sambhy et al. 2006; Yin and Deng 2015).

Why Antimicrobial Membrane Is Important?

Membrane biofouling due to the microbial growth and biofilm formation is one of the most challenging issues in membrane separation for water and

wastewater treatment (Zhu et al. 2010). This undesirable phenomenon decreases membrane permeability, reduces permeate quality, and increases energy consumption of the separation process. It is therefore critical to develop antimicrobial membranes that will most likely increase membrane efficiency and application duration. In addition, use of antimicrobial membrane is important to provide pathogen-free clean water.

Commonly Used Biocidal Agents for Membrane Modification

Biocidal agents that could be used for water treatment include quaternary ammonium compounds (QACs), metal ions or nanoparticles (NPs) such as silver (Ag) and copper (Cu), titanium dioxide (TiO₂), and so on.

QACs possess good antibacterial properties, low toxicity, environmentally friendly performance, and excellent cell membrane penetration properties (Song et al. 2011).

Silver ions/NPs and silver-based compounds have excellent biocidal properties and are widely used to prepare antimicrobial plastics, coatings, and wound and burn dressing, etc. They could inhibit the growth of microbes through multiple pathways. Firstly, released Ag⁺ ions could interact with disulfide or thiol groups of enzymes or DNA and then disrupt microbial metabolic processes, generate reactive oxygen species, or interrupt replication of DNA (Russell and Hugo 1994; Feng et al. 2000; Matsumura et al. 2003), leading to the damage or even the death of bacterial cells. Secondly, Ag NPs can attach to the surface of the cell membrane and disturb its proper function including destabilizing the outer membrane, collapsing the plasma membrane potential, and depleting the levels of intracellular ATP (Sondi and Salopek-Sondi 2004; Lok et al. 2006; Choi et al. 2008). Thirdly, Ag NPs with smaller particle size (1–10 nm) are able to penetrate inside the bacteria and cause further damage by possibly interacting with sulfur- and phosphorus-containing compounds such as DNA (Morones et al. 2005).

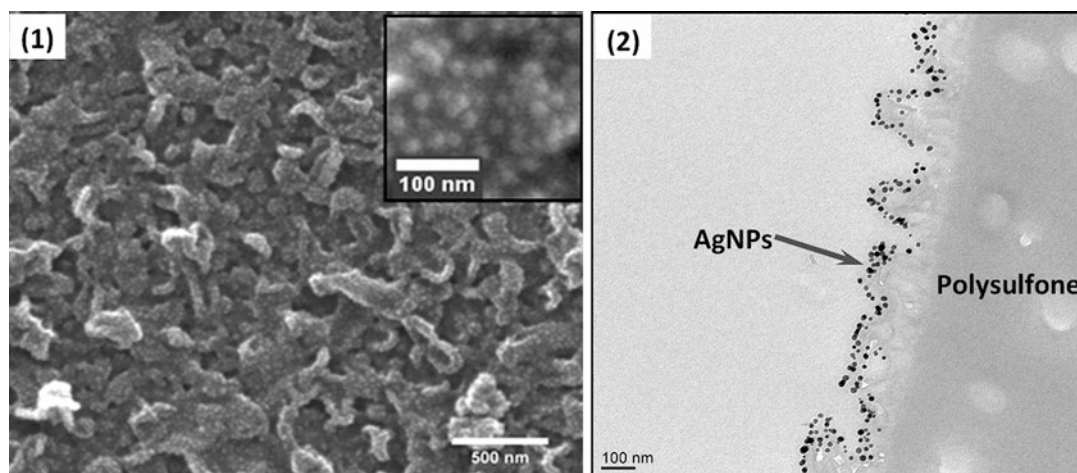
Recently, Cu is explored as an alternative of Ag due to its relatively low cost and decent biocidal property. The antimicrobial property of TiO₂ is driven by the photocatalytic reaction, where light irradiation is necessary.

Fabrication and Modification Methods

The antimicrobial functionalization of membranes could be implemented through procedures including blending, surface coating, or grafting. In the blending approach, biocidal agents are mixed with polymer solution during the membrane fabrication. In the coating or grafting approach, biocidal agents are attached onto membrane surface through adsorption, deposition, electrostatic attraction, or chemical bonding. For instance, Ag NPs or Cu NPs could be encapsulated in positively charged polyethylenimine (PEI) and then attached onto a negatively charged membrane surface (Mauter et al. 2011; Ben-Sasson et al. 2014). In order to improve the durability of antimicrobial function, Ag NPs can also be attached onto thin-film composite (TFC) membranes through chemical bonding, resulting in membranes with excellent antimicrobial properties and reduced membrane biofouling (Fig. 1, Yin et al. 2013).

Challenges

Antimicrobial membrane has attracted much attention due to its demonstrated resistance to membrane biofouling. However, several challenges need to be addressed in its practical applications. For long-term application, the loss of antimicrobial activity due to the depletion of biocidal agents or insufficient contact between bacteria and biocide caused by other foulants necessitates frequent recharging and cleaning of membranes. How to attach biocidal agents onto membrane and control their release in a most effective way should be further explored. For commercial applications, there is a need to consider cost-effectiveness of attaching biocidal



Antimicrobial Membrane, Fig. 1 SEM image of membrane surface (1) and TEM image of membrane cross section (2) (Yin et al. 2013)

agents onto a membrane and recharging them as needed.

Cross-References

- [Antifouling Membrane Surface](#)
- [Bacterial Biofilm Formation](#)
- [Cross-Linked Aromatic Polyamide Membranes](#)
- [Inorganic Fillers](#)
- [Mixed Matrix Membranes \(MMMs\)](#)
- [Nanocomposite Membranes](#)

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Antimicrobial Properties of Membranes

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Antimicrobial properties of membrane improve the membrane resistance to biological fouling. Antimicrobial properties can be provided to membranes by modification with different types of antimicrobial compounds, which can be divided into three categories based on their mechanisms of bacterial inactivation: biocide-releasing compounds, contact-action antimicrobial agents, and photocatalytic materials.

Biocide-releasing materials inactivate microorganisms by the release of biocide in the vicinity of the membrane. Common examples of biocide-releasing compounds used for antimicrobial coatings are silver nanoparticles, metal oxide nanoparticles, and polymeric capsules (Banerjee et al. 2011). Biocide-releasing materials may be included in the polymer solutions during fabrication or attached to the membrane via post-fabrication membrane modification. Embedding the biocide in the depth of the membrane may however limit its diffusion to the microorganisms and therefore decrease the antimicrobial activity of the modified membrane (Zodrow et al. 2009). To maximize the effectiveness of biocide release, surface attachment of biocide can be preferred (Mauter et al. 2011). A limitation to biocide-release materials is the eventual depletion of the biocide and loss of antimicrobial activity.

Contact-action antimicrobials are compounds that require direct contact with microorganisms for cell inactivation. Examples of contact-action antimicrobial materials are antimicrobial peptides, enzymes, polycationic polymers, and nanomaterials such as carbon nanomaterials (Banerjee et al. 2011). A common mechanism of cell inactivation by contact-action antimicrobial compounds is the disruption of cell integrity

upon interaction with cell wall components or penetration through the cytoplasmic membrane. This mechanism does not deplete over time and may be effective as long as a direct contact between the cell and the membrane surface is provided.

Photocatalytic materials generate reactive oxygen species upon exposure to visible or ultraviolet light. Their main applications in membrane processes are contaminant degradation and disinfection, where the membrane serves as a support to immobilize photocatalysts. The generation of reactive oxygen species by these materials causes bacterial inactivation by inducing oxidative damage to cell membranes, proteins, and nucleic acids, leading to cell death. Integration of photocatalytic materials into membranes therefore improves the antimicrobial properties of the membrane (Kwak and Kim 2001). Several compounds may be light-activated to generate reactive oxygen species. Among them are dyes like rose bengal, porphyrins, and toluidine blue and particles such as TiO_2 and fullerene (Banerjee et al. 2011). The most common photocatalytic material used in membrane processes is TiO_2 due to its low cost, durability, and self-cleaning properties.

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Antioxidant Recovery by Membranes

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Antioxidants and Membrane Processes

Antioxidants are natural or synthesized substances that inhibit or retard the oxidation of other molecules (fat, oil, food, petroleum product...) (Focke et al. 2012; Rozoy et al. 2012; Roblet et al. 2012). However, for natural antioxidants, which are present in complex matrices, their separation and purification are required. Indeed, they must be separated from the feedstock in order to increase their purity and antioxidant capacity.

Membrane processes are the main processes used for the separation of antioxidant molecules. Membranes are selective barriers that allow for the transmission of certain feed components while retaining other components. Membrane technology can be used to concentrate and/or selectively fractionate bioactive compounds with antioxidant activity from aqueous and alcoholic processing streams of products, by-products, and wastes from agro-food industry (Diaz-Reinoso et al. 2011). It is important to note that, when compared with other concentration methods (evaporation, spray drying...), during membrane processes the product is not subjected to high temperatures and there is no change in the physical state of the solvent, meaning that the functional properties of the compounds of interest are preserved and the process as a whole is energy saving (Negrao Murakami et al. 2011).

Membrane Processes and Applications to Antioxidant Recovery

On a large production scale, pressure-driven membrane technologies and electrically driven membrane technologies have been developed to

improve the efficiency of antioxidant production (Table 1).

Pressure-Driven Membrane Processes

Pressure-driven membrane technologies are often used in the food industry to isolate antioxidant molecules such as specific peptides or peptide fractions (Bazinet and Firdaus 2012; Pouliot et al. 2000; Tessier et al. 2006a, b; Vandanjon et al. 2009) and phenolic compounds (Nawaz et al. 2006; Kalbasi and Cisneros-Zevallos 2007; Mello et al. 2010; Tylkowski et al. 2010). Pressure is the main driving force for these processes. The pressure used depends on the pore size of the filtration membrane and has to be adjusted as a function of the concentration rate desired. Pressure-driven membrane processes comprise microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The solution properties, charges of ionic species and the type of membrane used, affect the behavior and the efficiency of the separation method (Martin-Orue et al. 1998). Working at low concentration is preferable to avoid the formation of a polarization layer which could affect selectivity of the membrane (Shahidi 2004).

For the separation of tocopherols and tocotrienols, only **MF** (de Souza et al. 2008) and **NF** (Subramanian et al. 1998a, b, 2003) were reported. For phenols recovery, **MF** was used on vegetation waters (VW) (Russo 2007) and pineapple juice (Laorko et al. (2010). The authors showed that MF did not affect significantly the pH, reducing sugar and acidity of clarified juice whereas the suspended solids and microorganism were completely removed. **UF** was studied on different sources such as olive mill wastewater (Russo 2007; El-Abbassi 2012), fruit juices (Borneman et al. 2001; Cassano et al. 2008; Laorko et al. 2010; Cissé et al. 2011; Conidi et al. 2011), grape seeds (Nawaz et al. 2006), and green tea (Li et al. 2005). **NF** was tested on roselle extract (Cissé et al. 2011), on mate (Negrao Murakami et al. 2011), on aqueous propolis extract (Mello et al. 2010), and on bergamot juice (Conidi et al. 2011). Organic acids such as Ascorbic, isoascorbic, folic, and citric acids can also be recovered by filtration process. Hence,

Antioxidant Recovery by Membranes, Table 1 Membrane processes for separation/concentration of different types of antioxidants

Driving force	Membrane process	Antioxidants	References
Pressure-driven membrane processes	Microfiltration	Tocopherols and tocotrienols	(de Souza et al. 2008)
		Phenols	(Russo 2007; Laorko et al. 2010)
		Organic acids	(Laorko et al. 2010)
	Ultrafiltration	Phenols	(Russo 2007; Laorko et al. 2010; El-Abbassi 2012; Borneman et al. 2001; Cassano et al. 2008; Cissé et al. 2011; Conidi et al. 2011; Nawaz et al. 2006; Li et al. 2005)
		Organic acids	(Cassano et al. 2006)
		Peptides	(Bouhallab and Touzé 1995; Lajoie et al. 2001; Vandanjon et al. 2007)
	Nanofiltration	Tocopherols	(Subramanian et al. 1998a, b, 2003)
		Phenols	(Cissé et al. 2011; Negrao Murakami et al. 2011; Mello et al. 2010; Conidi et al. 2011)
		Peptides	(Vandanjon et al. 2007; Fenton-May et al. 1971; Tessier et al. 2006b)
Electrically driven membrane processes	Electrodialysis	Phenols	(Bazinet et al. 2005)
		Organic acids	(Vera Calle et al. 2003)
	Electrodialysis with bipolar membranes	Organic acids	(Vera Calle et al. 2002)
	Electrodialysis with filtration membranes	Phenols	(Labbé et al. 2005; Bazinet et al. 2009, 2012)
		Organic acids	(Bazinet et al. 2012)
		Peptides	(Langevin et al. 2012)

MF was used for the recovery of ascorbic acid (Laorko et al. 2010), while **UF** was tested on kiwifruit juice to recover folic, ascorbic, and citric acids (Cassano et al. 2006). Concerning antioxidant peptides, they are separated into fractions using membranes in the range 1–10 kDa (Je et al. 2005; Jeon et al. 1999; Rajapakse et al. 2005). **NF** can be used to concentrate hydrolysates (Vandanjon et al. 2007; Fenton-May et al. 1971; Tessier et al. 2006b) whereas **UF** membranes with high MWCO (20–100 kDa) are adapted to the separation of peptides and nonhydrolyzed proteins or proteolytic enzymes (Bouhallab and Touzé 1995; Lajoie et al. 2001). On the other hand, **UF** membranes with intermediate molecular weight cutoffs (about 4000–8000 Da) allow hydrolysates to be fractionated with the result of enrichment in some ranges

of molecular weight (Vandanjon et al. 2007). The use of integrated membrane system (UF/MF/RO, MF/NF, ...) is becoming another real alternative to recover, purify, or concentrate antioxidants as it is established in some recent works (Paraskeva et al. 2007; Russo 2007; Garcia-Castello et al. 2010; Conidi et al. 2011; Diaz-Reinoso et al. 2011).

Electrically Driven Membrane Processes

Electrically driven processes, like electrodialysis (ED) and hybrid processes (ED with bipolar membranes (EDBM) and ED with filtration membranes (EDFM)), use ion-exchange membranes and/or filtration membrane to separate molecules (Bazinet 2005). The electric field is the main driving force involved in these processes. Molecular transfer is mainly due to the charge of the

molecule and the flux depends on the strength of the electric field (Poulin et al. 2007; Doyen et al. 2012).

Conventional **electrodialysis** has been tested as a mean of selectively extracting polyphenols from aqueous tobacco extracts (Bazinet et al. 2005). High polyphenol migration rates around 31.1–90.8 % were reported. **EDFM** a new electrically driven technology has been recently tested for the recovery of polyphenols. **EDFM** was used on green tea to perform selective extraction of catechins (Labbe et al. 2005) and on cranberry juice to enrich cranberry juice in its own natural phenolic antioxidant compounds (Bazinet et al. 2009, 2012). For organic acids having antioxidant properties, Vera Calle et al. (2003) were indirectly precursor in the use of **ED** for the recovery of citric acid. In all the deacidified juices, a decrease in the citrate and malate concentrations was obtained. Vera Calle et al. (2002) also tested the deacidification of clarified passion fruit juice, by electrodialysis with bipolar membrane (**EDBM**). Citric acid was formed in the concentrate compartment by citrate ions extracted from juice and protons provided by the BM separating the concentrate and electrode compartments. This configuration allowed the production of citric acid with 89 % purity. During **EDFM** of cranberry juice, Bazinet et al. (2012) observed that enriched juice concentrations in citric and malic acids decreased respectively of 7.3 % and 4.7 % resulting in a significant decrease of its sour taste intensity, a major problem for cranberry juice producer. However, the concentration in the raw juice was not significant due to the high ratio of raw juice/enriched juice. Very recently, a combination of UF membrane stacked in an electrodialysis cell was tested successfully for the selective separation of anionic and cationic antioxidant peptides (Langevin et al. 2012). The results showed only a significant increase in the antioxidant capacity for anionic peptide fractions recovered at pH 3 and pH 6 compared to the feed hydrolysate (Langevin et al. 2012). In the comparative study of Langevin et al. (2012), it was demonstrated that **NF** was more efficient in terms of mass flux than **EDFM** when compared on a same basis (membrane area, process duration), but

EDFM recovered larger range of peptide molecular weights and amount of polar amino acids.

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Antioxidants Recovery by Integrated Membrane Operations

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Natural antioxidants are synthesized by plants, microorganisms, fungi, and animals. They include phenolics, terpenes, proteins, peptides, and carbohydrates. Waste streams from the processing of agricultural feedstocks (residues from grape and wine, apple pomace, peels, woods, olives, seeds, leaves) are particularly attractive as sources of antioxidants.

Antioxidant compounds play an essential role in the human body to reduce oxidative processes. Therefore they offer interesting perspectives and opportunities in the production of dietary supplements and functional foods and potential utilization in pharmaceutical and cosmetic industries. However, since these compounds are generally present in complex matrices, extraction, separation, and purification methods are required in order to improve their purity. Extraction methods ideally should be nondestructive, time efficient, and suitable for producing high quantity of extract

which should be processed by selective techniques able to produce concentrated streams with enhanced antioxidant activity.

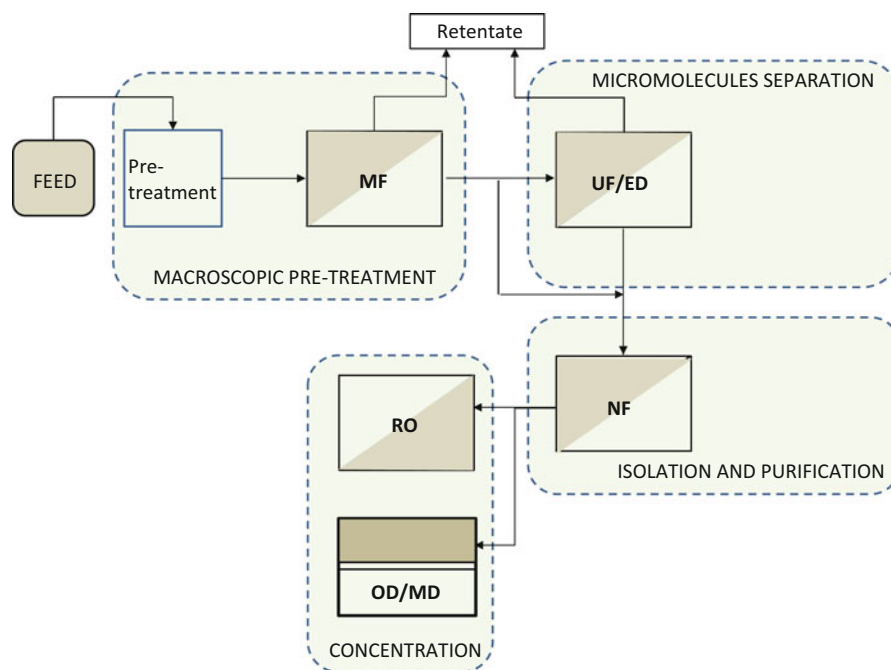
The recovery of antioxidants from agricultural by-products can be conducted according to the “5-Stages Universal Recovery Processing” strategy which includes (1) a macroscopic pretreatment, (2) a macro- and micro-molecule separation, (3) an extraction step, (4) an isolation and purification step, and (5) a product formation (Galanakis 2012).

Conventional extraction methodologies are based on the use of resins, organic solvents, enzymes, γ -irradiation, and heat treatment. These methodologies have drawbacks to some degree. For example, the extraction with organic solvents is characterized by safety problems (some of them are believed to be toxic), low efficiency, and time consumption; heat treatment results in pyrolysis; enzymes can be denatured in enzyme-assisted extraction; and γ -irradiation-assisted extraction is still unknown in terms of safety.

Membrane technologies are the main processes used at large scale for the separation of antioxidant compounds from different sources. They offer several advantages over conventional methods, in terms of high separation efficiency, low energy requirements, mild operating conditions, no additives, absence of phase transition, simple equipment, and easy scale-up. Pressure-driven membrane operations include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). These processes cover most of the “5-Stages Universal Recovery Processing” strategy since they can be used as macroscopic pretreatment (MF), in macro- and micro-molecule separation (UF), in purification (NF), and in concentration (RO).

These processes lead to the partial separation of the targeted compounds through size exclusion.

In addition to pressure-driven membrane operations, membrane distillation (MD), osmotic distillation (OD), and electrodialysis (ED) have emerged as new membrane technologies with great potential in integrated systems for the recovery of antioxidants from vegetable sources.



Antioxidants Recovery by Integrated Membrane Operations, Fig. 1 Schematic representation of antioxidants recovery by membrane operations (*MF*

microfiltration, *UF* ultrafiltration, *NF* nanofiltration, *RO* reverse osmosis, *OD* osmotic distillation, *MD* membrane distillation, *ED* electrodialysis)

In addition to RO, the concentration of bioactive compounds can be also performed by membrane distillation (MD) or osmotic distillation (OD). In these processes the driving force for the removal of water vapor across the pores of a hydrophobic membrane is given by a vapor pressure difference between the two sides of the membrane generated by a concentration (OD) or thermal (MD) gradient. Electrically driven processes, such as electrodialysis (ED) or a combination of ED with UF membranes (EDUF), have demonstrated very high selectivity for the separation of organic charged biomolecules. These processes use ion-exchange membranes and/or filtration membranes (such as UF) to separate molecules. The electric field is the main driving force involved in these processes. Molecular transfer is mainly due to the charge of the molecules and the flux depends on the strength of the electric field. In EDUF, fractionation of molecules is a function of their charges and molecular weights: according to the molecular weight cutoff of the UF membrane located in the cell,

low-molecular weight (MW) molecules cross the membrane, while higher-MW molecules remain in the feed.

Specific applications of pressure-driven and electrically driven membranes processes for the recovery of antioxidant molecules have been recently reviewed by Bazinet and Doyen (2016).

A schematic of integrated membrane operations, such as those previously described, for the recovery, separation, purification, and concentration of antioxidants, is depicted in Fig. 1. Such flow sheet is an example of flexible approach to valorize different agro-food by-products, as alternative to their disposal, within the logic of process intensification strategy.

A further improvement of the proposed integrated system has been recently investigated through the addition of a final step of membrane emulsification (EM) or biocatalytic membrane reactor (BMR) finalized to the formulation and valorization of antioxidant compounds in olive mill wastewaters (OMWWs) (Bazzarelli et al. 2015; Conidi et al. 2014).

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Antiscalant

► Scale Inhibitor

Antisolvent Membrane Crystallization

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This is an extension of the solvent evaporation membrane crystallization concept, where a porous membrane is used to dose the amount of antisolvent in the crystallizing solution, which has been proposed very recently (Di Profio et al. 2009). In this system, two operative configurations have been developed: solvent/antisolvent demixing and antisolvent addition membrane crystallization. In both cases, solvent/antisolvent migration occurs in vapor phase, according with the general concept of membrane crystallization and not by forcing it in liquid phase through the

membrane. The selective and precise dosing of the antisolvent, controlled by the porous membrane, allows a more fine control of the crystallizing solution composition during the process and at the nucleation point, with consequent advantages for the final crystal characteristics.

In solvent/antisolvent demixing configuration, a certain solute is dissolved in an appropriate mix of a solvent and an antisolvent whose composition is chosen in such a way that the solute remains indefinitely in the solution in the original conditions. When a gradient of chemical potential is generated between the two sides of the membranes, e.g., by a temperature difference, the solvent, which is supposed to have a higher vapor pressure than the antisolvent at the same temperature, evaporates at higher flow rate thus producing solvent/antisolvent demixing. As the amount of solvent in the mixture decreases, the lower solubility of the solute generates supersaturation and a phase separation occurs when the antisolvent exceeds a certain volume fraction. The requirements for this configuration are that: (i) the antisolvent and the solvent are miscible; (ii) the initial solvent/antisolvent balance in the mixture guarantees that the solute is under its solubility limit; and (iii) the solvent evaporates at higher velocity than the antisolvent. Crystallization of a solute from an aqueous/organic extraction mixture can be successfully carried out by this system.

In antisolvent addition configuration, a solute is dissolved in a solvent and then an antisolvent is gradually evaporated from the other side of the membrane by applying a gradient of chemical potential. As the antisolvent mixes with the solvent the solute dilutes but, at the same time, the composition of the mixture changes. At a certain point, the excess of antisolvent creates supersaturation and solute crystallization. This configuration requires that the antisolvent and the solvent are miscible. In this case, the compound to be crystallized can be soluble in aqueous solutions and poorly soluble in organic low boiling liquids.

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Antoine Equation

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Synonyms

Vapor Pressure–Temperature Relationship

History

Until the mid-nineteenth century, the prediction of the saturated vapor pressure of a liquid mixture or even of a pure liquid in relation with the temperature was not accurate despite the phenomena being studied long before the Middle ages. The Antoine equation, which solves this problem for pure components, is due to a French engineer (Louis Charles Antoine, 1825–1897) and was first published in “*Annales de Physique et de Chimie*” in 1891 (Antoine 1891). Antoine introduced an equation able to predict the vapor pressure of pure liquids (vaporization) and solids (sublimation). It is worth noting that this equation is still widely used today because of its accuracy. Wisniak (2001) has recently reviewed the historical development of the vapor pressure equations from Dalton to Antoine.

Phenomenon

The vapor pressure over a liquid is due to the thermodynamic equilibrium between the gas and

the liquid states of the component, which depends on the cohesive forces linking the molecules. In a closed cell, the vapor pressure of a pure component is a nonlinear relation of the temperature: the more the component is volatile, the more the vapor pressure is high.

Antoine Equation

For a given pure component in a closed cell, it calculates the saturated vapor pressure P (mmHg) with the temperature T (°C) as follows:

$$\log_{10} P = A - B/(T + C) \quad (1)$$

with A , B , and C being the Antoine coefficients, in mmHg and °C units, which are component-specific constants; e.g., for water : $A = 8.07131$; $B = 1730.63$ and $C = 233.426$ in the temperature range 1–99 °C.

Other forms of the Antoine equation can be deduced:

$$P = 10^{(A - B/(T + C))} \quad (2)$$

$$T = B/(A - \log_{10} P) - C \quad (3)$$

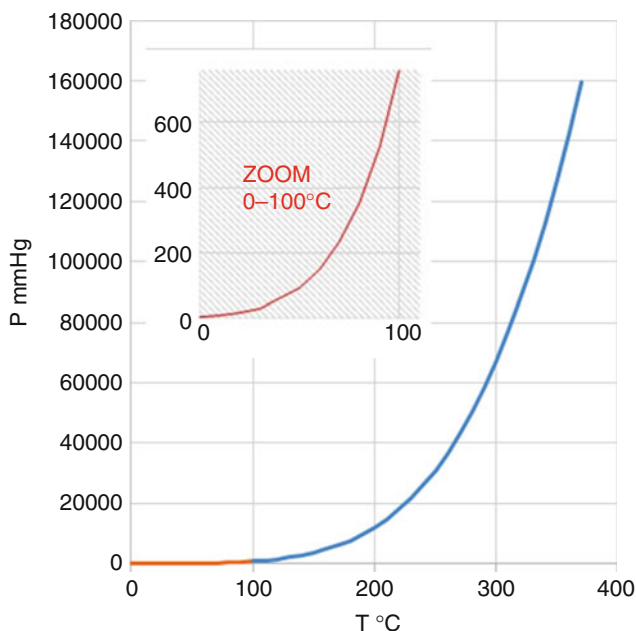
These equations fit very well for experimental vapor pressure data.

It is worth noting that the Antoine equation can also be used at high pressure or near the critical point. Indeed, for each component, two sets of parameters can be used according to the considered temperature range, i.e., either up to the normal boiling point or from normal boiling point to the critical point; in this last range, the Clausius-Clapeyron relation (Reid 1990) does not apply properly. In the case of pure water, in the temperature range 99–374 °C, the dedicated Antoine coefficients are $A = 8.140191$, $B = 1810.94$, and $C = 244.485$.

The extension (Wagner 1973) of the Antoine equation has been worked out to cover with a single set of parameters the whole temperature

Antoine Equation,

Fig. 1 Curves of $P_{\text{(sat) H}_2\text{O}}$ versus temperature; range 50–150 °C calculated with the Antoine equation



range going from the critical point to the triple point. This expression is required when computational techniques must be used.

On the other hand, a simplified equation using only two parameters was known to evaluate the vapor pressure; it was the August equation in which the parameter C is set to zero, thus assuming a temperature-independent heat of vaporization.

- For C coefficient, subtract 273.15 to take into account the modification of the temperature unit.

The Antoine coefficients have been tabulated for most of pure compounds. They can be obtained from various sources, including web access Data banks of Antoine Coefficients (visited June 2013).

Antoine Coefficients

Two systems of units can be used, either based on temperature and pressure, respectively, in °C and in mmHg or on K and Pa (SI system). Note that for historic reasons, the Antoine coefficients are still normally given based on the CGS system. Conversion from the historical system unit to the SI one can be made easily:

- B coefficient is the same in both systems;
- To get A coefficient in SI, add 2.124903 to the historical A; this value corresponds the pressure unit modification, i.e., to $\log_{10}(101325/760)$.

Example Calculation

This calculation has been done for water with the coefficients: $A = 8.07131$, $B = 1730.63$, and $C = 233.426$. The temperature validity range is from 1 °C to 100 °C.

- At $T = 50$ °C: $\log_{10}(P) = 8.07131 - 1730.63 / (50 + 233.426) = 1.9652$
- Hence, $P_{\text{(sat) H}_2\text{O}} = 92$ mmHg

The results shown in Fig. 1 and Table 1 correspond to water vapor pressure calculated with the respective sets of parameters of each domain with the Eq. 1. The discontinuity at 100 °C can be seen in the Table 1.

Antoine Equation, Table 1 Example calculation of $P_{(\text{sat})}$ H₂O; range 50–150 °C

T °C	log ₁₀ (P)	P mmHg	T °C	log ₁₀ (P)	P mmHg
50	1.9652012	92.30	100	2.8832575	764.29
60	2.1732982	149.04	110	3.0320002	1076.47
70	2.3676788	233.17	120	3.1745848	1494.81
80	2.5496558	354.53	130	3.3093227	2038.56
90	2.7203796	525.27	140	3.4368443	2734.29
100	2.8808629	760.09	150	3.5577142	3611.72
A = 8.07131	B = 1730.63	C = 233.426	A = 8.140191	B = 1810.94	C = 244.485

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Apple Juice and Membrane Operations

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Apple juice is one of the most popular juices worldwide. It approximately accounts for a 20 % of the juice market share, with a production of 1.5 million tons per year. Besides vitamins and minerals, apple juice is characterized by high levels of

phenolic compounds. Most part of the juice is consumed as clarified product.

Traditional methods of processing apple juice are based on the use of several batch operations that are labor and time-consuming. Typically, after preliminary operations (sorting, washing, and peeling steps), apple fruits are crushed and then pressed.

The juice is submitted to a heat treatment for 16 s at temperature of 72 °C to inhibit yeast growth and avoid fermentation. During the pressing step, pectinase is added in order to hydrolyze the pectin, reducing juice viscosity and making the product easier to filter. This process is performed at temperatures in the range of 40 to 50 °C for 1 h. After this step, fining agents such as bentonite, gelatine, or silica solution are added to the juice to improve the effect of settling.

After decanting, the juice is submitted to a precoat filtration, using filter aids, i.e., diatomaceous earths and perlite, to remove suspended solids, colloidal particles, proteins, and polyphenols.

The final product can be submitted to a concentration process by evaporation. It is generally performed in multiple effect evaporators at temperatures between 45 °C and 90 °C. During this step, undesirable alterations of the original aroma profile of the juice due to high operating temperatures are produced.

Membrane operations are competitive and attractive alternatives to the conventional treatments of apple juices. The advantages of using membrane technology, over conventional methods, are related to product costs, working conditions, environmental aspects, and product quality.

Apple juice clarification, stabilization, recovery of aroma, and concentration are typical steps where membrane operations as microfiltration (MF), ultrafiltration (UF), enzymatic membrane reactors (EMR), pervaporation (PV), reverse osmosis (RO), osmotic distillation (OD), and membrane distillation (MD) are successfully utilized.

The clarification of apple juice by membrane processes has been used commercially for over 30 years. In particular, the use of MF and UF represents a valid alternative to traditional methods in apple juice clarification and stabilization, resulting in increase juice yield, improved product quality, and avoidance of fining agents (gelatin, bentonite, and silica sol) and filter aids that are costly and present disposal problems.

MF or UF permits the removal of haze-forming components, such as suspended solids, colloidal particles, and proteins resulting in the production of superior juice quality. Turbidity values less than 0.1–0.2 NTU are typically obtained if compared to 2–5 NTU of conventional methods with fining agents.

Polymeric membranes made from polyethersulfone (PES), polyvinylidene fluoride (PVDF), cellulose acetate (AC), and polysulfone (PS) with pore size of 0.1–0.2 μm and molecular weight cutoff (MWCO) of 10–100 kDa are used for the clarification of apple juice.

Tubular, capillary, and plate-and-frame membrane modules are the most important configurations used at industrial level.

The clarified juice is usually concentrated in order to reduce storage, package, and shipping costs. In addition, concentrated apple juice is more stable, presenting higher resistance to microbial and chemical deterioration than the original juice as a result of water activity reduction.

Conventional methods of apple juice concentration, such as vacuum evaporation, usually employ high temperature to remove water. However, heat determines undesirable changes of juice quality such as color changes, off-flavor formation, and reduction in the nutritional value.

RO is a pressure-driven membrane process that can be used as an alternative process for apple juice concentration, as it does not involve phase change or the use of high temperatures. The main advantages of RO concentration are the attainment of high-quality products due to low operating temperatures, resulting in the retention of nutritional compounds and lower energy consumption.

However, the performance of RO membranes is limited by the osmotic pressures of the juice when the concentration reaches values of 25–30 °Brix; therefore, RO can be considered an advantageous technique as a pre-concentration step.

Polyamide and cellulose acetate RO membranes in both tubular and spiral wound configurations have been extensively used during the concentration of apple juice (Alvarez et al. 2002).

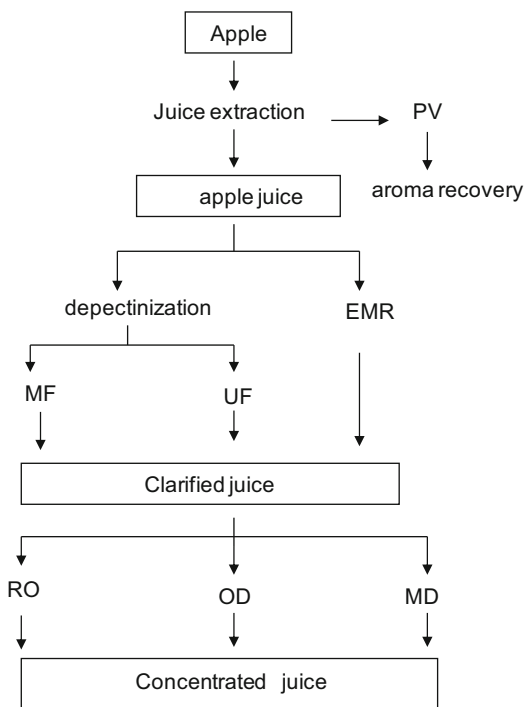
In order to overcome the limitation of RO in apple juice concentration, more recently, osmotic distillation (OD) and membrane distillation (MD) have been proposed as attractive membrane processes for apple juice concentration allowing very high concentrations (up to 65 °Brix) to be reached under atmospheric pressure and at room temperature, thus avoiding thermal and mechanical damage (Onsekizoglu et al. 2010).

These different membrane-based concentration techniques resulted very efficient in the concentration of apple juice, since the concentrated juice presented nutritional and sensorial quality similar to that of the original juice, especially regarding the retention of the bright color and pleasant aroma, which are lost during thermal evaporation.

Esters, aldehydes, and alcohols such as ethyl butanoate, ethyl-2-methylbutanoate, and hexanal are the main compounds which contribute to the aroma profile of apple juice.

PV constitutes a promising alternative to traditional techniques, such as distillation and partial condensation, for aroma recovery from apple juices.

Alvarez et al. (2000) proposed an integrated membrane process for producing apple juice and apple juice aroma concentrates.



Apple Juice and Membrane Operations, Fig. 1 Membrane operations for the treatment of apple juice

The process involves the clarification of raw apple juice by using an enzymatic membrane reactor, an RO unit to pre-concentrate the clarified juice up to 25 °Brix, a PV unit to recover and concentrate aroma compounds, and a final evaporation step to concentrate the juice up to 72 °Brix.

Rejection of aroma compounds in the PV step exceeded 90 % for most compounds considered. Organoleptic evaluation of the clarified and concentrated juice resulted excellent in terms of odor and flavor. The final products were more clear and brilliant than apple juice produced by conventional methods.

An economic evaluation of the integrated membrane system indicated a reduction of the total capital investment of 14 % and an increase in process yield of 5 % when compared with the conventional process.

A conceptual process design based on the integration of membrane operations in apple juice processing is depicted in Fig. 1.

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Application of FEEM to Monitoring Membrane Fouling

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FEEM refers to a fluorescence excitation-emission matrix that consists of a collection of intensity values for a group of excitation-emission pairs over a range of emission and excitation wavelengths. FEEM or fluorescence excitation-emission matrix is important in the context of monitoring membrane fouling because NOM, or natural organic matter, is a significant foulant in some cases for drinking water production, and some components of NOM are fluorescent. Fluorophores can be classified into two categories that can be described as intrinsic or extrinsic (Lakowicz 2006). Two of the three major fractions of NOM are intrinsic fluorophores: protein and humic substances. Other biological constituents that may end up in water may also be fluorescent and can contribute to the FEEM, but this will depend on the water source. For the protein component, the amino acids that can contribute to the fluorescent signal are tryptophan, tyrosine, and phenylalanine. The third component, the colloid/particulate matter, may be captured in the

Rayleigh scattering portion of the FEEM and is not necessarily fluorescent (Peiris et al. 2010a). This approach has the advantage that little or no sample preparation is required so analysis is rapid and can possibly be conducted online. Analysis of the FEEM data is required because it is rich in information, but various approaches are required to identify or correlate which components are contributing to fouling. Among the various approaches for analysis of the data is principle component analysis or PCA (Peiris et al. 2010b). The advantage of FEEM-based analysis is that this approach can provide potentially online information. Possible options that would allow data acquisition online would include flow through systems or fiber optic approaches. The data acquired can then be used in concert with instantaneous membrane flux or transmembrane pressure (TMP) measurements to garner more information related to the important foulants. Advantages of this approach are that water pretreatment strategies can be tuned or tailored to minimize the components that are contributing to the NOM-based fouling or to take appropriate action before membrane fouling becomes significant. Similarly, it may provide a useful technique for monitoring the membrane permeate for NOM constituents that may contribute to disinfection by-products (DBPs) which can serve as possible carcinogens.

Cross-References

- [Fouling in Membranes](#)
- [Irreversible Fouling](#)
- [Membrane Fouling](#)

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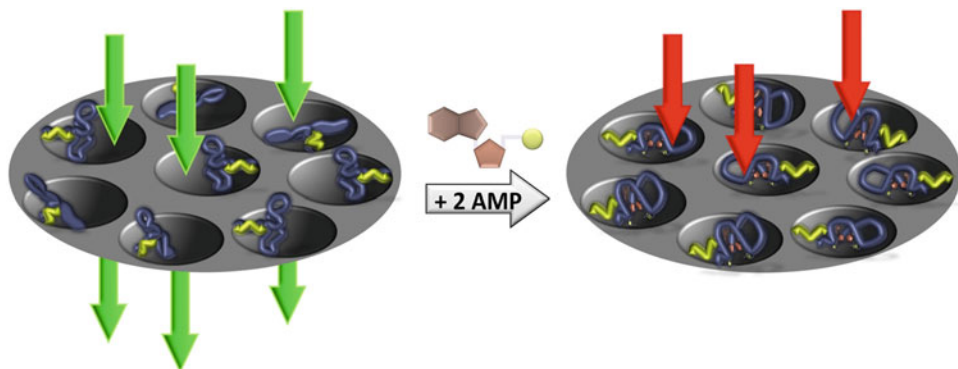
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Aptamer Membrane Functionalization

Thomas Schäfer

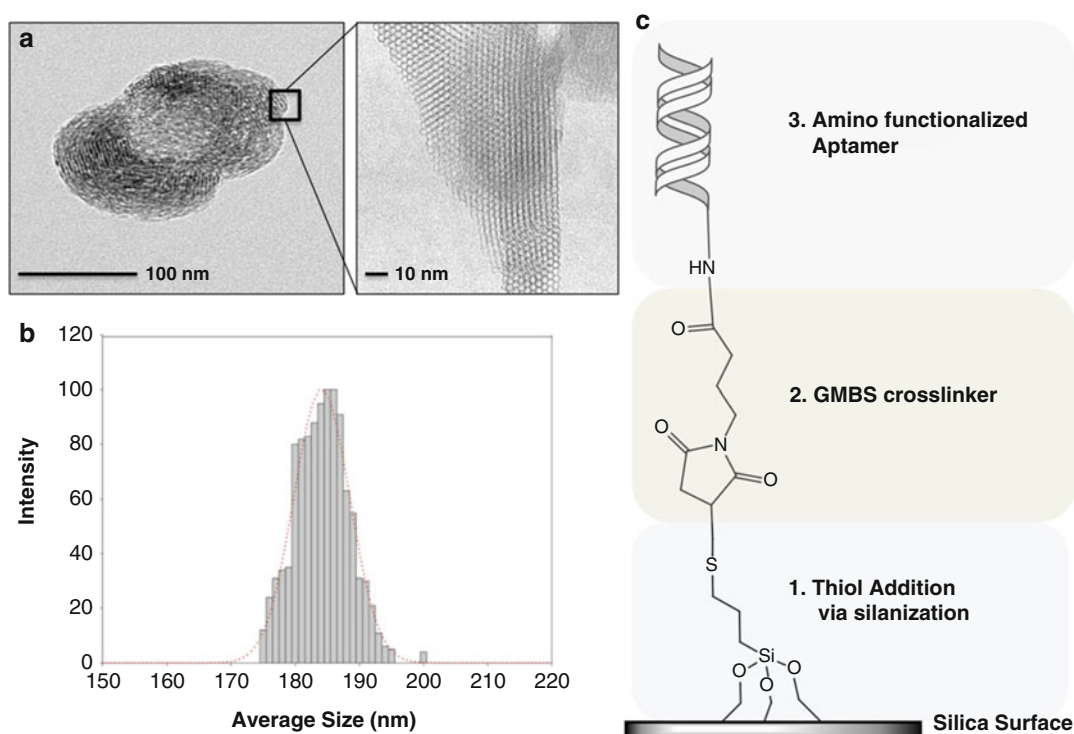
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Aptamer Membrane Functionalization. Aptamers can be incorporated into adequate porous membrane structures in order to obtain stimulus-responsive membranes whose permeability is modulated via a molecular recognition event. The concept relies on the fact that aptamers can recognize very specifically a molecular target, upon which a significant conformational change can occur if the aptamer is designed accordingly. In this sense, aptamer-modified membranes follow the concept “structure determines separation.” The stimulus-responsive membranes so obtained therefore do not require a bulk stimulus, such as a change in temperature or pH, which makes them particularly interesting for being employed in biomedical separations or DNA-based nanodevices (Bhattacharyya et al. 2013). Incorporating the aptamer into an adequate porous structure, the aptamer conformational change upon target recognition can give rise to a hindered pore flow, modulating in this way the overall membrane permeability. Aptamer-target interactions can be highly specific, target concentration dependent, and do not involve the formation of chemical bonds but are physical. As a consequence, membranes functionalized with aptamers change their permeability depending on the target concentration and in a reversible manner. Figure 1 depicts the concept of a membrane pore



A

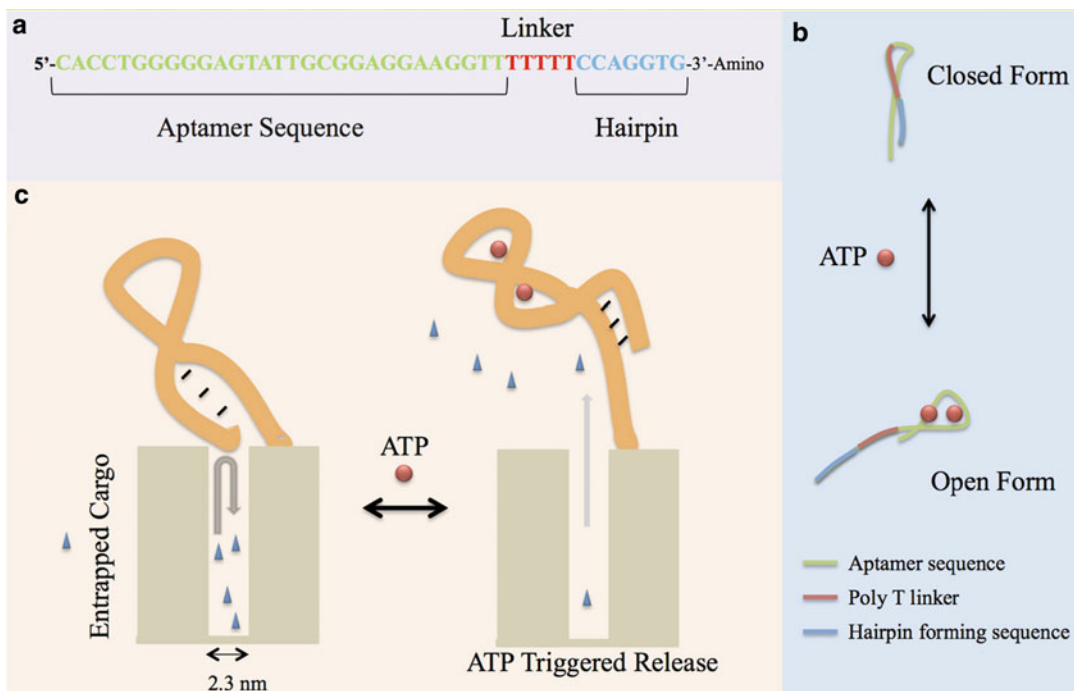
Aptamer Membrane Functionalization, Fig. 1 Scheme of a stimulus-responsive aptamer-functionalized membrane



Aptamer Membrane Functionalization, Fig. 2 Mesoporous particles (a), their size distribution (b), and the functionalization of mesoporous silica with an aptamer (c)

functionalized with a DNA-aptamer hairpin structure which changes its conformation upon a molecular stimulus such as adenosine 5'-monophosphate (AMP). In the absence of the target AMP, the aptamer-functionalized membrane pores remain

open and the membrane permeability maximum. Upon interaction with AMP, the aptamer undergoes a conformational change which significantly reduces the pore flow and, hence, overall membrane permeability.



Aptamer Membrane Functionalization, Fig. 3 Sequence of a DNA-aptamer hairpin that binds selectively to ATP (a), scheme of its conformational

change upon target recognition (b), and function to release in a reversible, specific, and concentration-dependent fashion cargo molecules (c)

For the conformational change to take effect, the pore diameter needs to be of the same order of magnitude. Therefore, mesoporous structures are preferably employed that furthermore possess a high degree of isoporosity. Aptamer-modulated pore flow has been thoroughly studied for mesoporous particles that are used as controlled delivery devices (Özalp and Schäfer 2011). Figure 2 shows the immobilization strategy for modifying mesoporous silica particles with aptamers and Fig. 3 the concept of how such an aptamer can serve as a reversibly opening “lid” in order to liberate cargo molecules upon target recognition (here: ATP).

A key parameter for the functioning of aptamer-functionalized membranes is the fine-tuning of the pore size within which the aptamer conformational change takes place. Pores too large would not result in any aptamer-modulated permeability, while pores too narrow would hinder the aptamer from freely changing its

conformation. It could be shown that the thickness change of a DNA-aptamer hairpin film amounts up to about 2 nm upon interaction with the target (Serrano-Santos et al. 2012). Hence, mesoporous structures with a pore diameter between 2 and 3 nm have been found to be a suitable base material for aptamer-functionalized particles and membranes (Özalp and Schäfer 2011).

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Aptamer Screening

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Aptamer screening or selection, also called systematic evolution of ligands by exponential enrichment (SELEX), is a combinatorial chemistry method by which aptamers (single-stranded DNA or RNA) are selected. SELEX is an evolutionary method driven by the binding of oligonucleotide sequences to a specific target based on their particular tridimensional structure, which confers high affinity and specificity. The selection process starts with a random oligonucleotide library consisting of a random region flanked by fixed primer regions required for PCR amplification. The random region confers outstanding variability, derived from the number of possible sequences in the library.

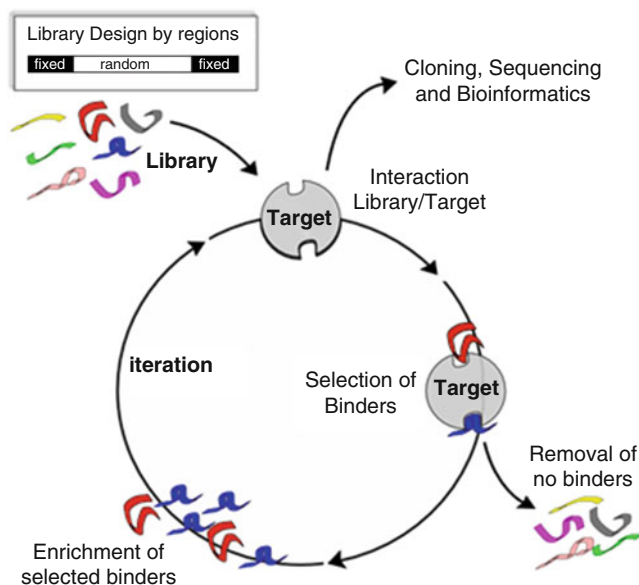
The variability of the library can be calculated with the expression 4^n , where 4 is the number of possibilities at each position (A, T, C, or G) and n is the length of the random region. SELEX allows the screening of oligonucleotide libraries

against a given target (i.e., protein, small molecules, or even whole cells) by an iterative process that involves (i) library/target interaction, (ii) selection of the sequences that bind to the target and removal of no binders, (iii) enrichment of the selected sequences by PCR, and (iv) after several screening rounds, cloning and sequencing to identify individual sequences. Finally, bioinformatic analysis is required to determine the most promising motifs or sequences. Next, the candidate sequences are evaluated to confirm their binding capability. SELEX technology could be compared to antibody production; however, SELEX offers interesting features that overcome some limitations of the antibody production, such as fast in vitro performance, no need for cells or animals, ease of selection under physiological or nonphysiological conditions, no limitation for target selection, and batch-to-batch reproducibility.

Since the first report of SELEX in 1992 by two independent groups (Tuerk and Gold 1990; Ellington and Szostak 1990), several modifications of the standard method have been reported to improve its performance. Nowadays, a significant number of aptamers have been selected and used as recognition molecules for environmental, food, diagnosis, and therapeutic applications (Fig. 1).

Aptamer Screening,

Fig. 1 Aptamer selection process from library



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Aptamers

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Aptamers (from Latin *aptus*, to fit) are artificial ligands binding with high affinity and specificity to their cognate target, selected through a Darwinian-like evolution method referred to as SELEX. Aptamers generally consist of structured single-strand nucleic acid molecules such as RNA and ssDNA; however, dsDNA and peptide aptamers have been described as well (Colas et al. 1996; Patel et al. 1997).

Aptamers can be selected against virtually any target and under nonphysiological conditions because no animal host is required. Hitherto, aptamers were selected against a broad range of target molecules, such as amino acids, peptides, proteins, drugs, organic and inorganic molecules, or even whole cells, with affinities often comparable to those of monoclonal antibodies.

The binding proprieties of aptamers are due to the formation of specific aptamer-target complexes stabilized by non-covalent interactions. The latter are a combination of van der Waals forces, hydrogen bonds, and electrostatic interactions. Binding of an aptamer to its cognate target can trigger an adaptive folding in which the target promotes and stabilizes the secondary and tertiary structures of aptamers. The dynamic conformations of free aptamers, consisting of labile knots, loops, and stems, turn into stable architectures within the aptamer-target complexes where noncanonical base pairing along with

intermolecular interactions creates unique binding pockets. Hence, along with a remarkable affinity, aptamers are generally characterized by high specificity. One of the most noteworthy examples is the anti-theophylline aptamer which can discriminate between theophylline and caffeine, two related molecules that only differ by a methyl group of the imidazole ring, having about 11,000 times higher affinity for the former. Similarly, aptamers have been reported to discriminate between enantiomers, macromolecules, proteins, and whole cells.

Apart from their high affinity and specificity, aptamers possess unique chemical and biochemical characteristics which clearly set them apart from other receptors. For example, aptamers are exceptionally stable: they may undergo denaturation, but the process is fully reversible within minutes; hence, temperature changes or long-term storage does not affect their functionality. Furthermore, the well-known chemistry of aptamers allows for site-directed chemical modifications and competitive production costs. New functional groups can be introduced a priori – within the SELEX process – using modified nucleic acid libraries or a posteriori modifying a selected DNA/RNA through chemical synthesis. While the first approach relies on the compatibility of the modification adopted with the enzymatic amplification necessary for selection, the latter approach is streamlined by detailed knowledge of the structure of both the aptamer and the aptamer-target complex. Since their first appearance in the early 1990s, aptamers have received constantly increasing attention, reflected in their use as diagnostic reagents and therapeutic compounds.

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Aquaporin-Incorporated Biomimetic Membranes

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Aquaporin, a transmembrane protein, has attracted attention globally since its serendipitous discovery by Peter Agre in 1992 (Agre 2006). Its facilitation in rapid and selective water transport has inspired many scientists to utilize this unique function for water treatment applications (Kaufman et al. 2010; Wang et al. 2012). Much effort has been devoted to build and overcome the challenges faced in fabricating the synthetic biomimetic membrane housing the water channel (Kumar et al. 2012). It is envisioned that this technology will bring about higher efficiency for desalination (Kaufman and Freger 2011) and hence lower cost.

Membrane Preparation Methods

Aquaporin-incorporated membranes can be prepared via the (1) Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) monolayer transfer techniques, (2) vesicle rupture of

aquaporin-incorporated materials onto a porous support, or (3) autopainting membrane (APM) method.

LB and LS monolayer transfer (Sun et al. 2012): The first monolayer of amphiphilic materials (lipids or copolymers) is deposited onto a solid support by the LB method. The second monolayer, which contains aquaporin-incorporated amphiphilic materials, is subsequently deposited onto the first layer by the LS method.

Vesicle rupture: Aquaporins are first incorporated into liposomes (Borgnia et al. 1999; Wang et al. 2011) or polymersomes (Kumar et al. 2007) through a typical transmembrane protein incorporation method (Borgnia et al. 1999). Subsequently, these aquaporin-incorporated vesicles are ruptured onto a porous support via charge interaction (Wang et al. 2011; Kaufman et al. 2010; Li et al. 2012) or covalent conjugation between the vesicles and the support (Wang et al. 2012; Zhong et al. 2012; Duong et al. 2012).

APM method: Free-standing aquaporin-incorporated lipid/polymeric membranes can be formed analogous to the conventional black lipid membrane preparation method (Hansen et al. 2009; González-Pérez et al. 2009). A mixed solution of aquaporins and amphiphilic materials is smeared across the hydrophobic array's apertures in electrolyte conditions. The membranes are spontaneously formed on the apertures at the interface of organic and aqueous phases.

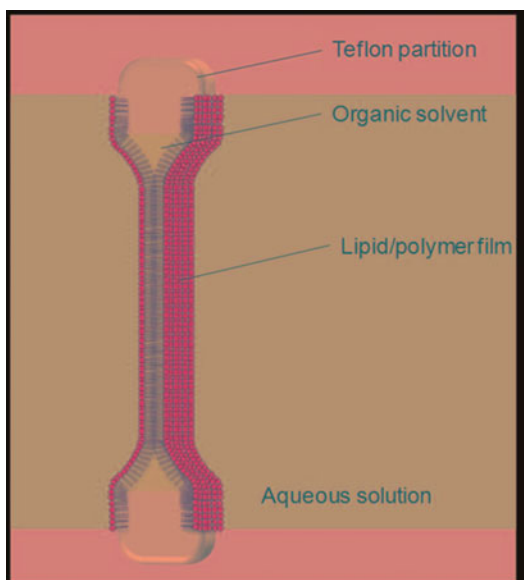
Aquaporin Biomimetic Membrane Designs

According to their conformations, the designs of aquaporin-embedded biomimetic membranes can be classified into two categories, namely, (1) free-standing lipidic/polymeric membranes (Fig. 1) and (2) supported lipidic/polymeric membranes (Fig. 2).

The free-standing lipidic/polymeric membrane is fabricated by assembling black lipid/block copolymer domains across multiple apertures in the ethylene tetrafluoroethylene (ETFE) scaffolds

(about 300 μm diameter each aperture) (Hansen et al. 2009; González-Pérez et al. 2009; Rein et al. 2011). This membrane array can be stabilized with the support of a highly permeable hydrogel layer (Lander et al. 2011; Ibragimova et al. 2012).

The supported lipidic/polymeric membranes with aquaporins have been designed for several applications, such as forward osmosis (FO), nanofiltration (NF), and reverse osmosis (RO). Detailed information on the materials and preliminary performance is summarized in Table 1.



Aquaporin-Incorporated Biomimetic Membranes, Fig. 1 Schematic graph of free-standing lipidic/polymeric membranes

Characterization of Water Transport Through the Aquaporin-Incorporated Membranes

The permeability of reconstituted aquaporin in vesicles is characterized mainly by the stopped-flow spectroscopy technique. In a stopped-flow experiment, the osmotic permeability P_f ($\text{m}^3/\text{m}^2/\text{s}$) can be calculated by using the equation (Borgnia et al. 1999)

$$P_f = k/C_{osm}V_w(S_o/V_o)$$

where k is the rate constant obtained from light scattering signal and $S_o(\text{m}^2)$ and $V_o(\text{m}^3)$ are the initial surface area and volume of the vesicle, respectively. V_w is the molar volume of water ($18 \times 10^{-6} \text{ m}^3/\text{mol}$) and C_{osm} is the osmolarity difference that drives the vesicle shrinkage.

The hydraulic permeability coefficient L_p (m/s/bar) represents the rate of water movement across a given area, per unit of osmotic gradient, and can be calculated from the equation (Hillyard 2012):

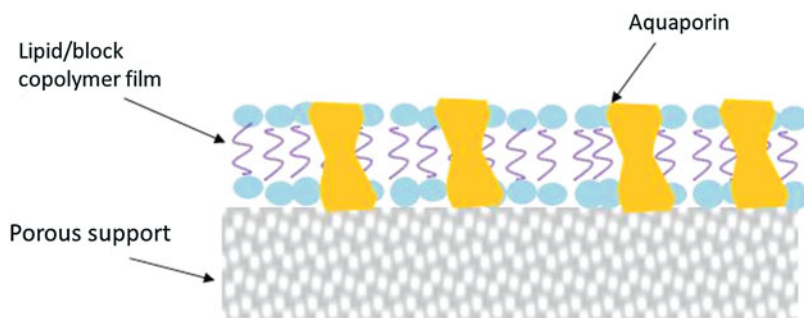
$$L_p = P_f V_w / RT$$

where R and T are gas constant and temperature, respectively. When the biomimetic membrane transforms from a sphere to a flat surface, the intrinsic water volume flux J_v (m^3/s) can be obtained by using equation (Hillyard 2012):

$$J_v = AL_p(\sigma\lambda RT\Delta C - \Delta P)$$

where A is the membrane area, in m^2 . σ is the reflection coefficient and is assumed to be 1. λ is

Aquaporin-Incorporated Biomimetic Membranes, Fig. 2 Schematic graph of supported lipidic/polymeric membranes incorporated with aquaporins



Aquaporin-Incorporated Biomimetic Membranes, Table 1 Demonstration of aquaporin-incorporated biomimetic membranes

Material of active layer and support	Membrane performance	Reference
PMOXA-PDMS-PMOXA ^a (with acrylate ends), aquaporin Z (molar ratio 1:50) Methacrylate-functionalized PCTE support (average pore size 50 nm)	FO Draw solution: 2M NaCl Feed solution: water Water flux: >100 L/m ² /h Salt reverse flux: <10 g/m ² /h	Wang et al. (2012)
PMOXA-PDMS-PMOXA ^a (with acrylate ends), aquaporin Z (molar ratio 1:50) Methacrylate-functionalized CA support (average pore size 19 nm)	NF Feed: 200 ppm NaCl Pressure: 5 bar PWP ^b : 34 L/m ² /h/bar Salt rejection: 32 %	Zhong et al. (2012)
PMOXA-PDMS-PMOXA ^a (with disulfide ends), aquaporin Z (molar ratio 1:100) Gold-coated porous alumina support (average pore size 55 nm)	NF Feed: 200 ppm NaCl Pressure: 5 bar Water flux: 8 L/m ² /h/bar Salt rejection: 45 %	Duong et al. (2012)
DOPC ^c and DOTAP ^d Aquaporin Z (molar ratio 1:200) Commercially available NF-270 support	RO Feed: 1 mM NaCl Pressure: 1 bar Water flux: 3 L/m ² /h/bar Salt rejection: 20 %	Li et al. (2012)

^aPoly(2-methyloxazoline-*b*-dimethylsiloxane-*b*-2-methyloxazoline)^bPure water permeability^c1,2-dioleoyl-*sn*-glycero-3- phosphocholine^d1,2- dioleoyl-3-trimethylammonium-propane (chloride salt)

the molecularity. ΔP is the hydrostatic pressure difference across the membrane, in bar. ΔC is concentration difference across the membrane, in mol/m³.

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Aquaporins (AQPs) or Water Channels

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Aquaporins (AQPs) or water channels are a family of integral membrane proteins that form hydrophilic pores in the cellular membrane. They are involved in the water transport through the membrane.

All cells depend on their ability to maintain water homeostasis. This is achieved through the action of aquaporins, membrane-bound water channels that facilitate water flow across cellular membrane along osmotic gradients, while excluding the passage of ions and protons. It is required for maintenance of the membrane potential and

intracellular pH. As with any membrane transport facilitator, aquaporins have evolved to be highly selective for their transported substrate without binding water so strongly that transport is inhibited. On the basis of their selectivity, aquaporins can be divided into two groups: the ordinary aquaporins, permeable to water only, and aquaglyceroporins which also permit transport of small solutes such as glycerol and urea. A number of other compounds have also been reported to be transported through aquaporins, including CO₂, NH₃, and arsenite (Kreida and Tornroth-Horsefield 2015). AQPs are transmembrane channels; thus the ability of a molecule to cross an AQP channel depends on its own characteristics (size, polarity, charge) and on the features of the AQP involved (Di Giorgio et al. 2014). They have a similar basic structure; AQPs are monomers of about 30 kDa and, in general, contain six membrane-spanning helical segments and two shorter helical segments that do not span the entire membrane. The AQPs generally form stable tetramers in membranes, although each monomer contains a separate water pore. High-resolution structural data show that the membrane-spanning helical domains surround cytoplasmic and extracellular vestibules that are connected by a narrow aqueous pore. Structural data and molecular dynamics simulations suggest that water molecules move through this narrow aqueous pore and that steric and electrostatic factors are responsible for the water selectivity of AQPs. The pore is less constricted in the aquaglyceroporins than in the water-selective AQPs (diameter of 3.4 Å versus 2.8 Å, respectively) and is lined by more hydrophobic residues (Papadopoulos and Verkman 2013). An important property of aquaporin-mediated water transport is its ability to be regulated in response to cellular or environmental signals. This is achieved by controlling water transport at the individual protein level through a conformational change, so-called gating, or by altering the aquaporin density of a particular membrane. These proteins are present in all kingdoms of life, demonstrating their central role in maintaining normal physiology of all organisms. The first member of this family, AQP1, was identified in erythrocytes in 1991.

This discovery led to homology cloning of hundreds of AQPs homologues from throughout the animal and plant kingdoms, as well as from lower organisms.

In humans there have been identified 13 aquaporins (AQP0–12) with specific organ, tissue, and cellular localization. Thus, different members of the AQPs family are expected to function in virtually all physiological processes that involve water transport across the membrane.

The AQPs are expressed in many cell types involved in fluid transport, including epithelia and endothelia in the kidney, lung, exocrine glands, eyes, and gastrointestinal tract. However, aquaporins are also expressed in cells that do not have an obvious role in fluid transport, such as erythrocytes and some leukocytes, adipocytes, and muscle. In addition, these are also expressed in astrocytes throughout the central nervous system and in supportive cells. Aquaporins have been linked to a number of pathological conditions, including brain edema, renal disease, obesity, and cancer, raising their attractiveness as drug targets.

Given the key role played by aquaporins in the kidney, for recovering water permeated together with other ions and molecules through the first part of the glomerulus, they have been investigated for developing biohybrid membranes able to desalinate seawater. The biohybrid membranes containing aquaporins showed very high water selectivity and permeability. Technological challenges for productive application include biohybrid membrane preparation on a large scale, aquaporin stability under operating conditions or during membrane module cleaning, and maintenance operation. Development of synthetic water channels mimicking aquaporins is a new strategy under investigation. Highly selective and permeable water channels are very interesting for the development of seawater desalination plant operating with very low energy input.

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Aromatic and Nonaromatic Separation by Membrane Operations

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Synonyms

[Dearomatization by membrane operations](#)

Efficient separation of aromatics/nonaromatics (generally referred to as dearomatization) is of great interest and significance to the chemical and petrochemical industries (Kung et al. 2010). Aromatic hydrocarbons such as toluene, benzene, ethylbenzene, and xylenes are important feedstock in petrochemical industry; therefore, purification of aromatics is desired after they are produced through catalytic reforming, cracking, or other processes (Sittig 1976). Nonaromatics also have a wide range of applications (e.g., solvents, fuels). They are generally derived from aromatics/nonaromatics mixed feed, which necessitates the separation of aromatic and nonaromatic hydrocarbons. For example, removal of aromatic hydrocarbons is needed to enhance the thermal and oxidation stability, viscosity, and color of lube oils. Aromatics such as benzene is carcinogenic; it is regulated by law that the levels of aromatics in petrol and solvents must be controlled (Singh et al. 2003). Removal of aromatics by-products will facilitate the improvement in the production efficiency of some petrochemical processes, such as ethylene production through steam cracking (Corma et al. 2005).

Presently, great interest from academia and industry is given to studying the separation of aromatic/nonaromatic by membrane process, which is pervaporation specifically due to the dense structure of its membrane capable of discriminating molecular-level difference as encountered in hydrocarbon mixtures. The separation in this process is based on the differential sorption and diffusion of permeating components inside membrane matrix, coupled with the intrinsic volatility difference of permeating components. It is the involvement of selective membrane that makes pervaporation process independent of the vapor–liquid equilibrium and therefore more energy efficient and environment friendly than classical distillation, rectification, extraction, and crystallization.

Numerous polymeric materials and some inorganic materials as well as their derivatives by chemical (e.g., grafting, cross-linking) or physical modifications (e.g., polymer blending, inorganic filling) have been applied in preparing pervaporation membrane for aromatics/nonaromatic separation (Smith et al. 2004). Aromatics have double-bond-related π -electrons, hence having affinity toward membrane matrix containing polar functional groups. Size selection also favors the aromatics in the separation of some aromatic/nonaromatic pairs. A typical pair is benzene/cyclohexane wherein the former has smaller molar volume. All of the organic and inorganic materials utilized show preferential transport toward aromatics. Carbon-modified nylon 6 exhibited an extremely high separation factor of more than 400. Commercialized polyvinyl alcohol composite membrane also presents recommendable separation factor and flux. As an effort toward practical application, integrally skinned asymmetric polymeric membranes for toluene/iso-octane separation were fabricated from blends of commercially available polybenzimidazole (PBI) and polyimide (PI) Matrimid using dry-jet wet spinning followed by non-solvent-induced phase inversion (Kung et al. 2010). The best performance achieved is a separation factor of 200 and a flux of 1.35 kg/m²-h in separating toluene/iso-octane (50/50 wt%). Separation factor for the selective transport of toluene increases with higher polybenzimidazole

content, while total flux is correspondingly reduced. This is because PBI has stronger polarity, tighter and more rigid structure, as well as enhanced anti-swelling property.

A pervaporation process alone might not be an economical choice for aromatic/nonaromatic separation. In the comparison among a conventional extractive distillation process alone, a pervaporation system alone, and a hybrid system consisting of the two processes in benzene/cyclohexane separation, it is found that a hybrid system is more economical than either of the two single processes (Rautenbach and Albrecht 1985). The feed solution used for the evaluation is 1:1 (mol/mol) benzene/cyclohexane, and the target is to separate this mixture into two streams: 99.5 mol% benzene and 99.2 mol% cyclohexane. In both extractive distillation process and hybrid process, furfural was used to break the benzene/cyclohexane azeotrope in the first stage. The product from this stage is a cyclohexane-rich stream and a mixture of benzene/furfural. The benzene impurity in the cyclohexane-enriched stream is then removed by pervaporation, and the benzene/furfural mixture is separated by distillation to get furfural and highly purified benzene. The advantage of hybrid system is more striking when higher purity is demanded of the products.

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Artificial Biological Membrane

► Bioartificial Synthetic Membrane

Artificial Blood Cell

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The expression *artificial blood* refers to artificial substitutes or artificial surrogates purposely designed in laboratory in order to mimic and fulfill two specific functions of the biological blood: the transport of oxygen and carbon dioxide throughout the body and the maintenance of the hemostasis inducing the blood clotting. Actually, the blood is a special type of connective tissue composed of four different components in charge of a variety of functions. The white cells, responsible for the immune defense; the red cells, responsible for the transportation of oxygen and carbon dioxide throughout the body; the platelets, involved in the hemostasis process; and the plasma, an extracellular component made up of water, salts, and various proteins that, along with platelets, encourages blood to clot. Actually, due to this complex composition, it is not possible to reproduce the blood artificially and only two of its components are laboratory designed: **the red blood cells and the platelet substitutes**. The artificial blood products have advantageous characteristics nowadays:

- They are safe and biocompatible and lacking of the membrane antigens; therefore they are usable for all patient blood types.
- They are able to transport oxygen throughout the body and release it where needed.
- They possess a great level of safety. They can be processed by filtration and pasteurization to remove all disease-causing agents such as viruses and microorganisms.

- They have a long shelf life. Unlike donated blood that breaks down after 1 month, artificial blood can be stored for over a year or more and it can be stocked and easily shipped where needed (Suman 2008; Cohn 2000; Nucci and Abuchowski 1998; Lesley 2001).

A brief history. Though popular folklore suggests that Maya Empire was trying to find a blood substitute, it is only after William Harvey discovered and described the blood pathways and circulation throughout the body, in 1616, that medical practitioners tried numerous substances such as milk, beer, plant resins, urine, and animal blood as a substitute for blood. Therefore, the first successful human blood transfusion was done in 1667. Only in 1868, researchers found that solutions containing hemoglobin isolated from red blood cells could be used as blood replacements. Therefore, the most important turning point in the development of artificial blood was made in 1883 and 1890s with the development of the Ringer's solution and the discovery by Karl Landsteiner of the human blood groups (A, B, AB, and O) according to the capacity of their red cells to express on their membrane surface specific antigens (Suman 2008; Nucci and Abuchowski 1998).

As already said, there are two different products under development as blood substitutes. They differ primarily in their functions: they carry oxygen or induce the blood clotting.

Red blood cell substitutes. They are classified in hemoglobin-based and perfluorocarbon (PFC)-based substitutes. **Hemoglobin-based products.** Derived from different sources (animal, human, recombinant) all hemoglobin products carry oxygen by taking advantage of the natural hemoglobin function. The natural hemoglobin products are obtained from human or animal blood. The human substitutes, in particular, are derived from blood and red cells collected during plasma donations. The synthetic products, on the contrary, are the results of amino acids specific combinations or the outcome of the recombinant biochemical technology, which allow to derive hemoglobin harvested from an *E. coli* bacteria strain. Independently on the sources, the protein breaks down easily into

smaller, toxic compounds. Then once obtained, it must undergo purification and partial modification in order to decrease (i) the rapid formation of dimers and monomers that freely diffuse into renal tubules causing renal failure and (ii) its strong affinity for factors (i.e., NO) causing vasoconstriction, hypertension, and bradycardia. Among the strategies employed to stabilize hemoglobin the main important are the chemically cross-linking molecule processes and the encapsulation technology. Polyethylene Glycol-Modified, Liposome-Encapsulated Hemoglobin, and Polymersome-encapsulated hemoglobin have been produced and commercialized (Enzon and APEX Bioscience) for the treatment of cancer and stroke patients and for treatment of hypotension induced by septic shock respectively (Chang 1998). Moreover, hemoglobin products covalently cross-linked with small bridges of sugar molecules showed not to induce vasoconstriction in phase III of clinical trials (Gould and Moss 1996; Danielson et al. 1997).

Perfluorocarbon (PFC) products. PFC-based solutions are synthetic hydrocarbons with halide substitutions able to dissolve up to 50 times more oxygen than plasma. These biologically inert materials allow to avoid the spreading of infectious disease via a blood transfusion. Nevertheless, they are not soluble in water solution and require to be emulsified in oils or lipids before being injected into patients' blood. Despite that a special product, developed by the PFC therapeutics, is currently in phase III of clinical trials for use in cardiac and general surgical patients, currently these substitutes showed to have a short duration of action, about 24 h, to be very expensive, and to cause some adverse reactions associated with their long-term usage. Their prolonged administration can cause several adverse reactions such as the increase of the blood pressure and of the pancreatic proteins, the gastrointestinal dysmobility, thrombocytopenia, flu-like syndrome, and a quite important oxygen toxicity (Suman 2008; Cohn 2000; Lesley 2001).

Platelet substitutes. These artificial products are very different from those already described. Classified in Platelet-Derived Products and

Platelet substitutes, they represent an essential component of the thrombogenic response to bleeding through the adhesion to the damaged vessel lining and releasing several coagulation factors. **Platelet-Derived Products.** Frozen platelets and cold liquid-stored platelets have been tested since 1950s in order to develop a treatment for thrombocytopenia. Despite being the only alternative to fresh platelets in clinical use, disadvantages as expensiveness with respect to the fresh platelets, morphological defects, and lower functionality directed the research toward new discoveries. The **Lyophilized platelet products** were developed since 1950s and are currently under animal trials. They are obtained by fixing human platelets in paraformaldehyde prior to freeze-drying them in an albumin solution with no influences on the adhesive properties of the cells. The **Platelet microparticles** are microvesicles formed spontaneously during the storage. Deriving from the platelet membranes, they showed similar hemostatic properties as intact platelets. Cypriss Bioscience developed **Infusive Platelet Membranes** (IPM; Cyplex, Cypriss Bioscience) using outdated human platelet that are purposely fragmented, virally inactivated, and lyophilized (Lesley 2001). With a shelf life of over 2 years these products are in phase II of clinical trials and appeared to be able to stop the bleeding in the 60 % of the patients resulted refractory to platelet transfusion due to the immune response to HLA or platelet antigens, with no adverse effects or risks of thrombosis. In order to overcome the disadvantages of the platelet processing, storage, and shelf life **Platelet Substitutes** have been proposed. The **Red cells with surface-bound fibrinogen or RGD peptides** have been subjected to numerous studies. Fibrinogen is a free molecule able to bind activated platelets together through the multiple Arginine-Glycine-Aspartate (RGD) sequences. Bounding to the surface of autologous erythrocytes (red blood cells), fibrinogen, or the RGD fragments, the "thromboerythrocytes" obtained showed to be hemostatically effective in some animal models of thrombocytopenia. Other important products are the **Fibrinogen-coated albumin**

microcapsules/microspheres. These are coated with fibrinogen of the human protein albumin. Two preparations have been evaluated in preclinical trials: SynthocytesTM (Andaris Group Ltd, Nottingham, UK) and ThrombospheresTM (Hemisphere, Irvine, Calif). The latter, due to their smaller mean diameter, showed in vivo to have a long duration of action. Last, two **Liposome-based agents** have been studied: the *plateletsomes*, which are lipid vesicles with platelet glycoproteins on their surface, and the *factor Xa* with phospholipid vesicles. Both demonstrated to be hemostatically effective in vitro and in some animal models, but problems of high toxicity must be overcome in order to pass the clinical trials.

Despite that numerous new discoveries and products showed to be useful as blood substitutes, the current artificial blood technology is limited by the short-term shelf life, the costs, and the toxicity problems clinically proved. Then new materials able to carry oxygen in the body and to induce the blood clot must be found and longer-lasting products should be developed (Suman 2008; Lesley 2001; Lee and Blajchman 1998).

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Artificial Brain Model: Biohybrid Membrane System

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Artificial brain, in membrane operation, is a biohybrid membrane system which provides suitable conditions for the creation of a biomimetic microenvironment for neuronal tissue engineering resembling in vivo neuronal tissue properties and functions.

In the last decade, neuronal cell behavior on biomaterial such as membrane has become of great interest since it offers the advantage of developing neuronal tissue that may be used for the in vitro simulation of human brain function substitute. This could provide further insights not only into the cell but also in developing therapies in neurodegenerative disorders such as Parkinson's or Alzheimer's diseases. A biohybrid system using neurons could also represent a useful instrument for predictive drug testing or constitute a future model of a bioneuronal network device. To accomplish this task the artificial membrane must exhibit a specific micro-architecture able to stimulate neuronal regeneration, therefore supporting axonal regrowth and affecting cellular orientation and differentiation in a positive way.

This biohybrid artificial system consisting of neurons and membranes offers a valuable tool for studying neuronal cell behavior and fundamental questions in neuroscientific research, and it also could be used in a wide range of biotechnological applications.

Several works in the literature show evidence that semipermeable polymeric membranes in flat and hollow fiber configurations, thanks to their highly selective structural, physicochemical, and transport properties, allow the successful in vitro reconstruction of neuronal tissue reproducing a tissue model for studying metabolic diseases and

drug effects (De Bartolo et al. 2008; Zhang et al. 2005; Morelli et al. 2014; Piscioneri et al. 2015).

For typical neuronal tissue-engineered constructs, the properties of the material components relevant to the tissue response include the surface microgeometry, the MWCO, the electrical properties, possibly the bioactive factors that are loaded and sustainably released through the channel wall, and the degradation rate for biodegradable materials. The wettability of the membrane surface has proved to be a factor that affects the growth of neurons modulating the adsorption of adhesion proteins contained in the culture medium or secreted by cells that mediate the adhesion of cells to the substrate.

Advances in polymer chemistry have facilitated the engineering of synthetic membranes that can be specifically manipulated with regard to their physical and mechanical characteristics, which may affect the interactions with cells.

The influence of topographical features on neuronal cell adhesion and differentiation has been studied by using patterned adhesive areas that provide only a fraction of the surface for cell adhesion while the rest is cell repellent or by using contact guidance cues in combination with also nerve growth factors or an electric field. Topographic guidance of neurite outgrowth has been explored in vitro with a culture substrate containing etches, microchannels, nanotubes, or microgrooves. Micro-patterned biodegradable poly(L-lactic acid) membranes directly improved the guidance of neurite extension and thereby enhanced their orientation with a consequently highly ordered neuronal cell matrix, which may have strong bearings on the elucidation of regeneration mechanisms (Morelli et al. 2010).

Hippocampal neurons exhibited a different morphology in response to varying the properties of the membrane surface. Indeed, cells grown on the smoother membranes such as fluorocarbon (FC) and PES membranes displayed a large number of neuritis with consequent formation of bundles. The density of axonal network increases the neurites to become more elaborate and highly branched on the smoother surfaces.

The importance of FC membrane culture substrates toward the highlighting of the effects of highly preferred GABA_AR α 2,5 agonists and inverse agonists on the successful elongation of neuronal processes and transcriptional activities of hamster hippocampal Gluergic cells was demonstrated for the first time (Giusi et al. 2009).

A biohybrid system composed of neuronal cells and silicon-supported nanoporous membranes has been designed to facilitate control of the biochemical environment of neuronal networks with cellular resolution. Nanoporous membranes may be used to interface with biological materials in a biohybrid system, for example, as an artificial chemical synapse interface (Wolftrum et al. 2006).

Compared to traditional two-dimensional (2D) culture systems, 3D in vitro cultures of neuronal cells appear to better mimic in vivo neuronal microenvironments representing a great potential for building 3D neuronal circuits as well as for creating tissue-based biosensors and for promoting systemic restoration of severe nerve injuries. In this context, several studies have been performed toward the determination of differences between 2D and 3D environments for neuronal function in order to provide great benefit to neuroengineering efforts. Recently, a complete 3D neural tissue-like structure has been assembled in vitro using primary hippocampal cells and PAN HF membranes. As a consequence, this advanced model system could allow the mimicking of hippocampal neuronal events in order to study natural neurobiological properties of these cells, such as memory and learning processes, or the induction of disease pathologies, allowing testing of new therapies on the resolution of these states (Morelli et al. 2012).

In the last decade, with rapid advances in biomaterial technology, several types of natural and synthetic biodegradable polymer, including collagen, chitosan, poly(glycolic acid), poly(L-lactic acid), poly(L-lactide-co-glycolide), poly(caprolactone), and polyurethane, have been reported as suitable for nerve regeneration, although the ideal physicochemical compositions, surface structure, and functionalization of such

materials have not yet been found. It was recently reported that polycaprolactone-based membranes successfully supported outgrowth and differentiation of human neuronal cells (Morelli et al. 2015).

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Artificial Kidney

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Artificial kidney, a synonym for hemodialyzer, is an extracorporeal device through which blood may be circulated for removal of elements that normally are excreted in the urine.

The artificial kidney is used to rid the blood of metabolic products, to correct electrolyte-water and acid-alkaline balances in acute and chronic renal insufficiency, to remove dialyzing toxic substances in cases of poisoning, and to remove excess water in cases of edema. In 1913 the American scientist Abel created an apparatus for dialysis that was the basis for the artificial kidney; Dr. Willem Kolff, a Dutch physician, constructed the first functioning artificial kidney. He treated his first patient in 1943, and in 1945 he was first able to save a patient's life with hemodialysis treatment.

The artificial kidney operates on the principle of the dialysis of substances through a semipermeable membrane. Dialysis is a result of the differences in the concentrations of substances in the blood and in the dialyzing solution, which contains glucose and the principal electrolytes of the blood in nearly physiological concentrations without containing any of the substances that must be removed from the body (urea, creatinine, uric acid, sulfates, phosphates). Proteins, formed elements of the blood, bacteria, and substances with a molecular weight of more than 30,000, do not pass through the membrane. During hemodialysis the patient's blood is drawn off through a catheter by a pump from the inferior vena cava and passed inside the chambers of membranes of the dialyzer; these chambers are washed outside by the dialyzing solution, which is supplied by another pump. Partially purified, the blood is returned to one of the surface veins.

Artificial Functional Organ

► Membrane Artificial Organs

The membrane used during hemodialysis has evolved significantly since the earliest reports. Early membranes were natural materials, such as cellulose, or simple synthetic compositions, such as polysulfone, with symmetric structures and good performance for small solute passage (Fleming 2011).

However, these membranes include significant interactions with the complement pathway and immune response. Modifying the hydroxyl groups on cellulose membranes gives similar performance characteristics and less bioactivity and includes cellulose diacetate and hemophan membranes. With improvements in chemical engineering and manufacturing, cellulose-based membranes have yielded to synthetic membranes. The most popular membranes in use today are polyacrylonitrile and polysulfone; however, polyamide, polycarbonate, and polymethylmethacrylate are available. These materials have improved biocompatibility and reduce complement activation; however, they may enhance protein adsorption to the membrane in the absence of further modification. Despite the improved compatibility of synthetic membranes, the most recent large review does not demonstrate benefits conveyed by biocompatibility. The ultrastructure of membranes is predominantly the capillary design, or hollow fiber structure, in which blood flows through a series of small tubes held together in a bundle. This allows for a low-resistance, high surface area membrane. Membrane properties such as charge, wall thickness, and pore size affect function. The radius of the pore is related to the ultrafiltrate flow through the membrane, but overall fluid transfer is a function of the mean pore size. The number or density of pores and the radius of the pore affect solute transfer in diffusive clearances. Membrane characteristics such as flux and permeability to water are determinants of pore characteristics and wall thickness (Vigano et al. 2008).

As dialysis membrane technology has improved, high-flux membranes with larger pore sizes have been developed to allow greater clearances of larger retention molecules with

reduced induction of inflammatory mediators. While observational studies suggest that high-flux hemodialysis is associated with lower and dialysis-related amyloidosis, individual randomized controlled trials have not confirmed that high-flux hemodialysis improves clinical outcomes. High-flux dialysis membranes have larger pore sizes that may increase transportation of dialysate impurities or contaminants from the dialysate to the bloodstream even when the dialysate quality complies with acceptable standards, although some evidence suggests that high-flux membranes may actively absorb endotoxins and impede their back transfer from dialysate into the bloodstream (Palmer and Strippoli 2013).

Although dialysis is currently an available treatment for chronic renal disease, it replaces only the filtration function of the kidneys, and thus, it is associated with a number of complications and is not a permanent solution. Kidney transplantation performed in a heterotopic location is the only definitive solution for end-stage renal failure. A potential solution to ease the demand for donor kidneys may be the use of tissue engineering techniques that could be used to develop functional kidneys. A primary challenge in renal tissue engineering, however, is the production of tissues with the functional complexity required for kidney transplantation. The first step in achieving this aim could be to produce acellular kidney matrices for use as biological scaffolds that support cell growth and facilitate new tissue formation by potentiating cell–cell interaction. Several groups have used different perfusion-based decellularization protocols to produce naturally derived kidney scaffolds (Arenas-Herrera et al. 2013).

In the last decade, several studies have been performed on the development of the implantable artificial kidneys, but these studies reported only developmental concepts, in vitro or in vivo studies using small animals. It is difficult to control certain research aspects of an implantable artificial kidney to a preclinical level, and these aspects include long-term maintenance of the

antithrombogenic properties of the systems and each of its components, and the function of an implanted, miniaturized system, whose function must be maintained for a year's duration. Further progress in nanotechnology and biotechnology is required to realize a treatment with an implantable kidney (Saito et al. 2011).

New directions in dialysis research include cheaper treatments, home-based therapies, and simpler methods of blood purification. These objectives may be probably obtained with innovations in the field of artificial kidney through the utilization of new disciplines such as miniaturization, microfluidics, and nanotechnology. This research may lead to a new era of dialysis in which the new challenges are transportability, wearability, and why not the possibility to develop implantable devices (Ronco et al. 2011).

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Artificial Liver, Membrane Operations

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The expression of artificial liver defines all the supporting membrane systems able to substitute or integrate the liver functions when it reaches the 30 % critical threshold of the normal hepatic activity. The liver is the biggest glandular organs in the human body. Placed in the upper section of the abdominal cavity, this dark red organ is well known to be able to self-regenerate from partial injuries doubling its mass in 1 day. Therefore, acute or chronic hepatic insufficiencies caused by viral pathology, drug abuse, intoxications, or pathological decompensation can result in severe liver failure (LF). Though implying the inability of the liver to completely carry out its metabolic, excretory, and detoxifying functions, both the acute and chronic hepatic insufficiency (ALF, ACLF) can potentially be reversible if one third of the organ is still functioning; then liver activity can return to good levels. However, the LF leads to an accumulation of water-soluble and albumin-bounded toxins that cause encephalopathy and a multi-organ dysfunction. The solely long-term therapy to stem a hepatic insufficiency is the orthotopic transplantation that ensures a notable recovery of hepatocytes in number and functionality. Actually, due to the limited number of donors, only a narrow circle of patients in waiting list can be transplanted according to the severity of their disease. Thus, in order to improve patients' prognosis and survival, artificial extra-corporeal liver assist devices have been developed either "bridging" the patient to transplantation and temporarily supporting the failing organ until it is able to regenerate. Basically, three different types of supportive therapies are nowadays available: bio-artificial, artificial, and hybrid liver support

Artificial Liver

► Bioartificial Liver

systems. Therefore, between them, the artificial systems are the most used in clinic due to the lower costs and their easier handling. Artificial liver support systems are cell-free membrane devices aimed to temporally replace native liver detoxification functions through processes of adsorption and filtration in order to improve the clinical state of the patient. The most of artificial liver devices use membrane separation associated with columns or suspensions of sorbents (e.g., charcoal, anion-exchange or cation-exchange resins) that selectively remove toxins and/or regenerate dialysate or plasma filtrate (Carpentier et al. 2009; Naruse et al. 2007). Conventional dialysis techniques, such as hemofiltration, hemodialysis, or hemodiafiltration, have been used for the removal of the low molecular weight water-soluble metabolites. The *hemodialysis* allows to remove water-soluble metabolites, to re-equilibrate the acid-basic and the electrolytic values in the blood, and to reduce also the ammonia concentrations. The *hemofiltration* is carried out by filtrating cellulose or polysulfone membranes with a MWCO of 50 KDa. These membrane devices remove toxic and natural substances through connective transport allowing to partially recover from the hepatic encephalopathy. The *hemoperfusion* is performed through extracorporeal devices constituted by active charcoal adsorbing elements covered by a cellulose or polysulfone hemocompatible film. Adsorbing a variety of water-soluble toxins in the low and middle molecular weight range, the hemoperfusion has a significant disadvantage; in fact it has been demonstrated that the resulting patient's plasma can be highly impoverished of important biological substances causing important decompensation in patients' metabolism. In order to improve the specificity of the detoxification process, *membrane reactors containing immobilized enzymes* have been developed. Hepatic enzymes are definitively linked onto hollow fiber membranes or enclosed in microcapsules and showed to be able to enhance the recovery of the patients' mental state; hence, the percentage of surviving patients does not increase, and the clinical application is very limited. The *plasma exchange/plasmapheresis* is another

artificial support system for treating the LF. The cellular components of the blood are separated from the plasma using a hollow fiber filter (cellulose diacetate or polyethylene) able to remove toxins and supply lacking components as albumin or coagulation factors. However, this method has a disadvantage: it requires a large plasma stock with ensuing higher costs and bears the risk of infections. Moreover, most of the toxins that accumulate in the plasma of patients with liver insufficiency are protein bound; then these methods are not able to adequately eliminate them. This is the reason why new dialysis systems have been developed using albumin as scavenger to clear the toxins involved in the physiopathology of the failing liver. Between the different albumin dialysis modalities, the single-pass albumin dialysis (SPAD) has shown some positive results. The patient's blood passes a high-flux dialysis membrane, while an albumin solution streams counter-directionally to the filtering blood membrane, accepting toxins from the plasma. Therefore, the system works at a very high cost due to the high concentration of albumin needed in the dialysate to perform the plasma detoxification (Naruse et al. 2007; Onodera et al. 2006). At present, there are only two artificial extracorporeal liver support systems used in clinic: the *Molecular Adsorbents Recirculating System* (MARS[®]) from Gambro and *Fractionated Plasma Separation and Adsorption* (FPSA), which was designed by Fresenius Medical Care (Bad Homburg, Germany) and commercialized as Prometheus[®] (Carpentier et al. 2009; Evenepoel et al. 2006).

MARS is the most used artificial liver support system. Introduced in clinics in 1993, it consists of three components: (A) a conventional dialysis machine that guides the extracorporeal blood circuit (MARSFLUX), (B) a supplementary device for the albumin circuit made of two different adsorption columns (MARS AC250, MARS IE250), and (C) a dialysate circuit for low flux dialysis (Rademacher et al. 2011). *How it works*: the patient's blood is pumped in the blood circuit throughout a double-lumen central venous catheter. Here a first column, the MARSFLUX system, contains a polysulfone membrane with MWCO of

50 KDa that filters the blood and allows the passage through the membrane of the water-soluble molecules and the free toxins, retaining the albumin due to its higher dimension. In the meantime, the second circuit pushes in counter direction with respect to blood flux, a 20 % albumin solution that induces the dissociation of the protein-bounded toxins freeing the albumin of the plasma. The dialysate albumin, now saturated, is then restored passing through two adsorption columns in the second circuit: the MARS AC250 filled with active charcoal that retains high molecular weight molecules (bilirubin) and the MARS IE250 filled with the anion-exchange resin cholestyramine that retains the negative-charged molecules. Albumin solution of the second circuit is then restored and can be used for a new cycle of treatment. The MARS is recommended for treating both acute and chronic liver failure, despite the survival of patients is only partially increased. Therefore, many positive clinical results have been recorded for the patients in the last years such as the increase of the arterial pressure values and the systemic vascular resistance index, the attenuation of hyperdynamic circulation, and the significant decrease not only for bilirubin but also for creatinine and urea (Evenepoel et al. 2006; Rozga 2006).

The Prometheus artificial system realizes the combined removal of the albumin-bounded and the water-soluble toxins by means of adsorption and fractionated plasma separation. It was developed by Falkenhagen in 1999, and the system is based on FPSA combined with hemodialysis and consists of two circuits (Falkenhagen et al. 1999). In the first one, the blood is collected through the double-lumen catheter and allowed to flow through a polysulfone membrane. Its MWCO of 250 KDa allows either the free toxins or the plasma albumin-bounded toxins to pass through the membrane reaching the second circuit. Here the plasma is purified by a direct adsorption process into the same two columns of MARS: the anion-exchange column and the neutral resin column. Then the blood is recombined with the non-treated fraction and dialyzed completely in a high-flux device for the water-soluble molecules' removal (Evenepoel et al. 2006; Rozga 2006).

In the last decades, other dialysis albumin circuits have been developed for LF treatment, such as the *continuous veno-venous hemodialysis* (CVVHD) and the *continuous veno-venous hemodiafiltration* (CVVHDF); therefore, though being able to decrease the load of water-soluble toxins, they cannot provide the complete plasma treatment. The last available artificial liver is named *selective plasma filtration therapy* system (SEPET). In this system, the patient's blood passes through a single-use cartridge constituted by hollow fibers with MWCO of 100 kDa allowing molecules with a molecular weight close to 100 kDa to pass the membrane in only limited amounts, while albumin, HGF, and several clotting factors are retained. Main characteristic of this process is that a plasma fraction is completely discarded during the filtration procedure. This fraction contains accumulated small molecular weight toxins and free pro-inflammatory cytokines; then, to replace the fluid loss, a mixture composed of electrolyte solution, human albumin solution, and fresh frozen plasma is added to the system and collected to the patient's blood. This SEPET system is designed for use with any commercially available kidney dialysis unit and/or plasma apheresis system utilizing hollow fiber cartridges (Carpentier et al. 2009; Rozga 2006). Many other attempts in developing artificial liver systems are conducted nowadays in order to improve methods and clinical results. The ultimate goal is then to develop a liver support device that will grant patients a substantial survival benefit compared to standard intensive care now available.

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Artificial Lung

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The artificial lung is a medical device used to take over or supplement the function of the lung which is to oxygenate the blood and remove carbon dioxide.

Such a device can replace entirely the pulmonary gas exchange or assist the deficient gas transfer capacity of the natural organ, either temporarily, with the hope that the healing process will eventually repair the diseased organ, or permanently, when irreversible lung damage leaves the patient permanently disabled.

Artificial lung can be used as a bridge to lung transplantation, as a support device immediately post-lung transplant, and as a rescue and/or supplement to mechanical ventilation during the treatment of severe respiratory failure (Diaz-Guzman et al. 2013; Javidfar and Bacchetta 2012).

Current artificial lungs are also known as blood oxygenators and are modules composed of bundles of hollow fiber membranes designed to bring blood and gas phases in intimate contact separated by only the thin walls of the hollow fibers.

Membrane oxygenators can be used in two principal modes: to imitate the function of the lungs in cardiopulmonary bypass (CPB) and to oxygenate blood in longer-term life support, termed extracorporeal membrane oxygenation (ECMO). A membrane oxygenator consists of a thin gas permeable membrane separating the blood and gas flows in the CPB circuit; oxygen diffuses from the gas side into the blood, and carbon dioxide diffuses from the blood into the gas for disposal.

Preliminary efforts to design, fabricate, and test membrane artificial lungs have been reported since the 1950s. The early artificial lungs used relatively impermeable polyethylene or Teflon homogeneous membranes, and when more highly permeable silicone rubber membranes were introduced in the 1960s (and as hollow fibers in 1971), the membrane oxygenator became commercially successful. The introduction of microporous hollow fibers with very low resistance to mass transfer revolutionized the design of membrane modules, as the limiting factor to oxygenator performance became the blood resistance (Martin and Zwischenberger 2013).

Current designs of oxygenator typically use an extraluminal flow regime, where the blood flows outside the gas-filled hollow fibers, for short-term life support, while only the homogeneous membranes are approved for long-term use.

The key design considerations in blood oxygenators include minimizing the resistance to blood flow, reducing the priming volume, ensuring easy debubbling at setup, and minimizing blood activation and thrombogenicity.

The fabrication or wrapping of the fiber bundle in a blood oxygenator can be important as the geometry obtained impacts diffusional boundary layers, secondary flows, and gas exchange efficiency.

Looking ahead, current challenges in bioartificial lung engineering include creation of ideal scaffold materials, differentiation and expansion of lung-specific cell populations, and full maturation of engineered constructs to provide graft longevity after implantation in vivo (Sond and Ott 2012).

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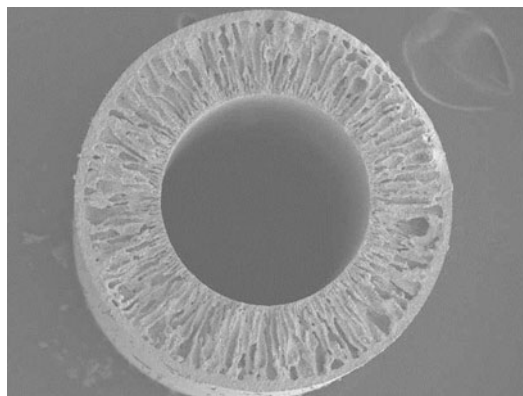
Assisted Transport

► Facilitated Transport

Asymmetric Ceramic Hollow Fiber Membranes

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Asymmetric ceramic hollow fiber membranes are ceramic tubes with outer diameters typically ranging from 0.5 to 2 mm, utilized for separation processes. To be classified as asymmetric, a hollow fiber must have a nonuniform cross-sectional structure consisting two or more different morphologies. They may be formed from a wide range of ceramic materials depending on their purpose and may be either dense or porous according to the type of separation process for which they are designed. When combined together in a module, hollow fiber geometry gives rise to extremely high membrane surface area per volume leading to compact membrane module designs. Asymmetric membranes offer improved performance by combining a thin separation layer with a support layer which has high permeability. Although asymmetric structures can be achieved by depositing additional layers on a symmetric ceramic hollow fiber formed by screw



Asymmetric Ceramic Hollow Fiber Membranes, Fig. 1 An asymmetric aluminum oxide hollow fiber micro-filtration membrane with an outer diameter of 1.8 mm

extrusion, the most common method of fabrication involves the incorporation of phase inversion to create asymmetric structures during the extrusion process. In this method, a mixture of polymer binder and ceramic material, suspended in a suitable solvent, is extruded through a spinneret into contact with a fluid that leads to precipitation of the polymer phase. As the polymer binder precipitates, the polymer-ceramic suspension is converted into a polymer-ceramic mixed matrix ceramic hollow fiber precursor. The precursor is then heated to remove the polymer binder and consolidate the ceramic material by sintering to yield the final product. Very small hollow fiber diameters can be achieved using this fabrication technique with asymmetric cross-sectional structures consisting of conical micro-channels as well as a porous ceramic matrix (Fig. 1). Moreover, multiple layers can be extruded simultaneously to form asymmetric cross-sectional structures which also contain layers of different materials.

Asymmetric ceramic hollow fiber membranes can be broadly categorized as either porous or dense. The former operate on a size exclusion basis usually at low to moderate temperatures and are commonly fabricated from inert ceramic materials such as aluminum oxide. Asymmetric structures such as that shown in Fig. 1 (Kingsbury and Li 2009) are prepared in a single step and

consist of a support layer formed from micro-channels and an outer porous separation layer. The development of asymmetric morphologies such as that shown in Fig. 1 allows for filtration membranes with high flux to be fabricated in a cost-effective way, with the additional benefit of integrated separation and support layers, leading to a robust and durable structure. Dense asymmetric ceramic hollow fiber membranes operate at higher temperatures with separation occurring by lattice diffusion. Membranes fabricated from proton conducting, ionic conducting, and mixed ionic and electronic conducting materials have a number of potential applications such as oxygen separation from air, solid oxide fuel cells, and the partial oxidation of methane to synthesis gas. For example, an asymmetric hollow fiber oxygen separation membrane can be formed from a perovskite material, by extruding a hollow fiber in which a region of micro-channels supports a thin outer oxygen separation layer (Zydorczak et al. 2009). The micro-channels formed during the extrusion process provide mechanical strength while at the same time greatly reducing the resistance to oxygen permeation compared to a symmetric hollow fiber structure. Asymmetric multilayer structures formed by co-extrusion have been developed for solid oxide fuel cells and membrane reactor applications in which each layer has a different function. Examples include the co-extrusion of an anode and electrolyte as an asymmetric hollow fiber in a single step (Othman et al. 2010), and the co-extrusion of a dual-layer hollow fiber membrane reactor for partial oxidation of methane to synthesis gas comprised of a dense oxygen separation membrane on a porous catalytically active support (Wu et al. 2011).

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Asymmetric Hollow Fiber Membranes

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The asymmetric membranes can be formed into different geometries such as the flat sheet and the hollow fibers, by choosing the fabricating or casting equipment. Hollow fibers have annulus cross sections with the inner and outer circular skins of the membranes being concentric. The outer diameter of a hollow fiber is less than 1 mm. Their advantages associated with practice usage include large membrane area per unit volume, self-contained mechanical support, good flexibility, and easy handling during the module fabrication and in the operation, etc. (Matsuura 1994, Peng et al. 2012). These facts have contributed to the lower fabrication cost and higher-performance efficiency of hollow fiber membrane modules.

By far, the most technically used hollow fiber is produced by phase inversion: non-solvent-induced phase inversion (NIPS), (solvent) evaporation-induced phase inversion (EIPS), VIPS (vapor sorption-induced phase inversion), and TIPS (thermally induced phase inversion) (Ulbricht 2006). In single-layer hollow fiber asymmetric membrane formation by NIPS, there are two coagulations taking place in hollow fiber spinning (shell and lumen surfaces), while there is only one major coagulation surface for an asymmetric flat sheet membrane. The mass exchange between internal coagulation liquid and lumen surface for a hollow fiber starts immediately after liquid extrusion from the conduit of a spinneret. For the contact of shell surface of nascent fiber and the external coagulation bath, two

different concepts are used. In some cases, there is an interval between nascent membrane extrusion and immersing in the external coagulant. This contact at the external boundary could also synchronize with that at the internal boundary by directly immersing the spinneret inside the external coagulant. The former has a name of “dry-jet wet spinning.” The mass transfer associated with the dry step during the nascent fiber’s residence time in the air gap is short under commercial spinning conditions but important in membrane structure control. Solvent evaporation in the dry step can cause polymer concentration at dope/air interface increase. This situation is favorable for forming a relatively compact skin and is often practiced in fabricating membranes for gas separation or pervaporation. One can easily create this situation by making the temperature of the spin dope close to the boiling point of the volatile solvent or non-solvent (Jiang et al. 2004). Rheological aspect is another choice in fine-tuning hollow fiber membrane morphological characteristics to meet the requirement of separation tasks. Depending on the polymer intrinsic rheological characteristics, air gap and take-up speed are adjusted to deliver polymer chain orientation or more ordered arrangement along the elongation direction that improves selectivity of gas separation membranes (Kneifel and Peinemann 1992). Shearing effect that occurs inside the spinneret can also induce orientation, which motivates many design strategies of conduit channel near the exit (Widjojo et al. 2007).

Composite hollow fibers are mostly formed by dip coating, interfacial polymerization, etc., as an additional step to the porous hollow fiber formed by phase inversion. Presently, the type of dual-layer composite asymmetric hollow fibers produced by co-extrusion through a triple-orifice spinneret represents a new direction (He et al. 2002). Compared to the single-layer asymmetric hollow fibers, the dual-layer hollow fibers are more advantageous due to the following reasons (Jiang et al. 2009):

1. Material cost saving by more than 95 %
2. Possibility to employ brittle (engineering infeasible) but advanced material

3. By adjusting the dope solution concentration, hollow fibers with ultrahigh pressure resistance can be produced
4. The formation of composite membranes is more straightforward and cost effective
5. Higher fluxes are obtained by circumventing pore penetration occurring in dip coating.

Recently, an idea of immiscibility induced phase separation (I₂PS) was proposed (Ong and Chung 2013). Phase separation of two immiscible dopes renders the formation of a selective layer between the inner layer and outer layer. The degree of swelling of selective layer by feed liquid can be moderated as a result of its being shielded from direct contact with the feed mixture by the outer layer.

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Asymmetric Membrane

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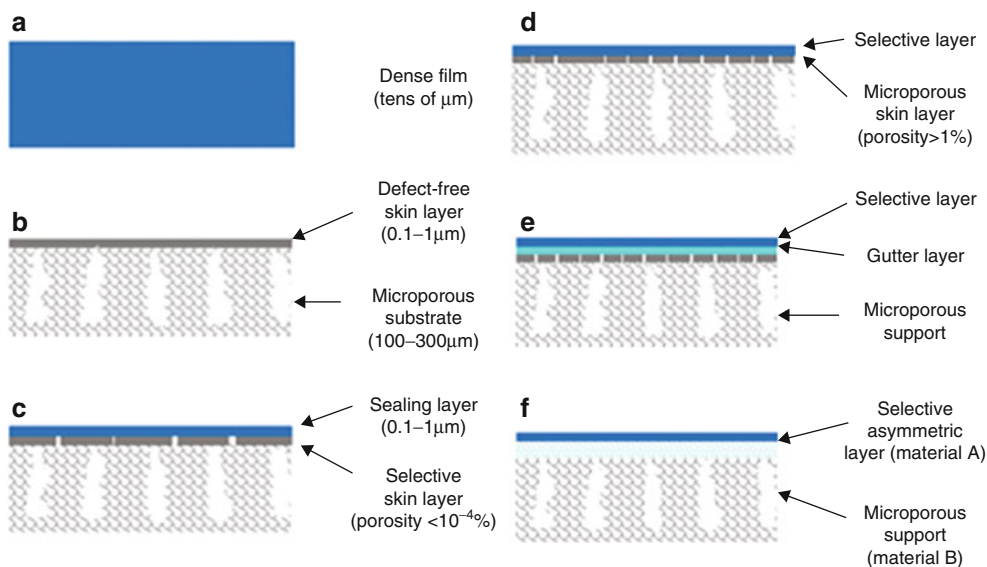
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For almost all the membrane process, flux is one of the essential process parameters. The advantages associated with high flux are small membrane area and efficient system footprint. These two factors are often considered by chemical engineers or managers in their decision-making about setting up processes using membrane separation. The thinner the required membrane structure, the higher the membrane flux. However, mechanical strength will be reduced with decreasing membrane thickness.

One of the solutions to this problem was asymmetric membrane. Loeb and Sourirajan in 1963 (Loeb and Sourirajan 1964) invented integrally skinned asymmetric membrane for reverse osmosis. They are produced by non-solvent-induced liquid-liquid phase separation processes, in which the entire structures are generated in one

step from one material. Phase inversion is a process wherein the thermodynamically stable polymer solution is converted into the instable one by changing dope composition. The resultant membranes exhibit graded morphology with a gradual transition from relative dense structure at one side of the membrane to fully porous structure on the other side, in consistence with the characteristics of phase inversion course. In a simplified manner, this type of membranes is often described as having a thin skin supported by a porous support. The thin skin layer carries out the separation, while the substrate generally presents negligible resistance to the transport of penetrants. This so-called skin layer is nonporous for gas separation, reverse osmosis, pervaporation, and nanofiltration membranes. There also exist several other techniques pertaining to phase inversion. They are thermally or pressure induced. The membranes generated have a rather isotropic cross-section morphology.

To fulfill the same target but avoid the disadvantages of the integrally skinned asymmetric membranes, a series of other types of membrane are developed. Figure 1 shows the schematic of the dense membrane and five principle types of membranes that are currently used (Paul and



Asymmetric Membrane, Fig. 1 Schematic of dense and asymmetric membranes. (a) Dense film, (b) integrally skinned asymmetric, (c) multicomponent ("caulked")

composite, (d) single-layer composite, (e) multilayer composite, (f) asymmetric composite

Yampol'skii 1994): (a) homogeneous dense membrane, (b) integrally skinned asymmetric, (c) caulked, (d) single-layer composite, (e) multilayer composite, and (f) asymmetric composite membranes. Usually, a homogeneous membrane is prepared through solution casting. This type of membrane is used for the lab-scale investigation to fundamentally understand the intrinsic properties of polymers. Various techniques are available in the formation of composite membranes. They can also be categorized as asymmetric membranes morphologically. The multilayer composite (Fig. 1d) is an extension of single-layer composite, and the asymmetric composite (Fig. 1e) is the combination of the integrally skinned asymmetric and composite approaches. In addition to decreasing selective layer thickness, one of the most attractive aspects of the composite membranes is their potential for minimizing materials' cost, because only the selective layer must use a high-performance while more expensive material. The freedom in material choice and membrane formation technique selection with composite membranes facilitates the development of organic/inorganic layered structure that efficiently combines the characteristics of single organic or inorganic material and expands the application area of membrane separation. The aforementioned asymmetric or composite structure can be formed into different geometries such as the flat sheet, the hollow fibers, etc., by appropriately choosing the fabricating or casting equipment.

Today, extensive knowledge exists on how to control the asymmetric membrane's structure including cross-section morphology by the selection of material and membrane formation conditions. The polymeric composite membranes are usually made by solution coating, interfacial polymerization, and plasma polymerization methods on the surface of a prefabricated porous support or by co-extrusion of two or more solutions (Ulbricht 2006). For composite membrane using inorganic materials, they are prepared by various techniques from solvent evaporation, in situ growth from solution, and other alternative methods (Gulianti et al. 2004). The work at commercializing asymmetric membranes, especially those having

nonporous skin, has been hindered by the difficulties of obtaining simultaneously the good selectivity and the high productivity. In other words, the intrinsic property of some advanced material cannot be expressed efficiently in their asymmetric membranes. Various physical or chemical treatments can make the skin layer more perfect (Jiang et al. 2009). One of the breakthroughs conquering this problem in the membrane development was made in 1980s by Henis and Tripodi (Henis and Tripodi 1980). Their invention of coating asymmetric polysulfone membranes with silicon rubber effectively sealed the pinholes and led to first generation of commercial gas separation membrane, Prism or Prism Separator.

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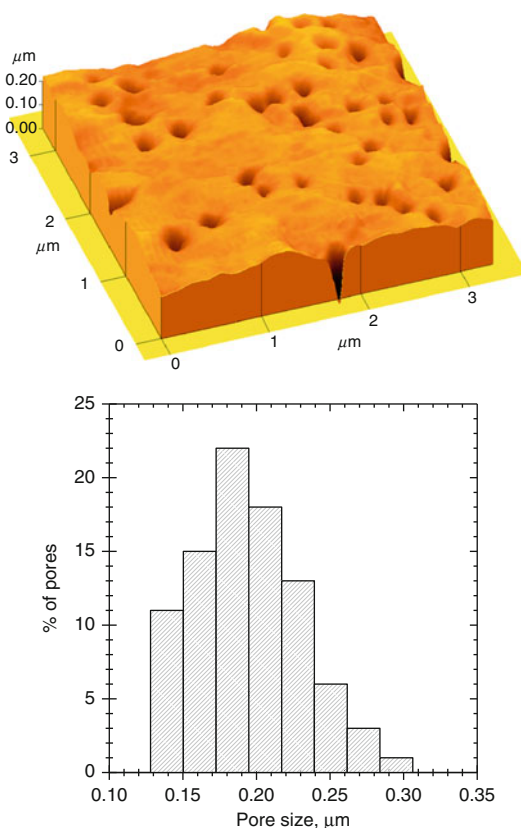
Atomic Force Microscopy (AFM)

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The atomic force microscope is a versatile tool increasingly used for the physical characterization of surfaces and is of great interest for the visualization and analysis of process surfaces including

those of membranes used for filtration. It is capable of resolving features from the micrometer down to the subnanometer scale and can operate in air and liquid environments, allowing membranes to be studied in environments matching those encountered during their operation (Hilal et al. 2004; Hilal and Johnson 2010), which allows assessment of effects of, for instance, pH, ionic strength, and effects of additives on membrane structure, a feature not available with other high resolution imaging applications. In addition, the surface needs no special preparation, providing it remains clear of unwanted contamination, and does not need to be electrically conductive, limitations found with some imaging techniques.

The AFM consists of a sharpened probe mounted at the end of a flexible cantilever. The tip of the probe is then used to “feel” the underlying membrane surface, producing a three-dimensional map of the sample topography. There are three basic imaging modes: contact mode, where the tip maintains constant contact with the surface, while feedback loops adjust its height to maintain cantilever deflection and hence force; tapping mode, where the cantilever is vibrated close to the resonant frequency and intermittently contacts the surface with decreased lateral forces compared with contact mode; and noncontact mode in which the probe tip interacts with attractive forces very close to the surface but is kept away from hard repulsive interactions. Noncontact mode is capable of extremely high resolution but is the most difficult to attain in practice. From the imaging data, several quantitative parameters of interest to membrane technologists can be obtained including: surface roughness, pore size, pore-size distribution, as well as showing in fine detail the morphology of fouled and unfouled membrane surfaces and the effects of chemical modification of membrane surfaces (Johnson et al. 2012; Kochkodan et al. 2013). Figure 1 shows a typical image of a cyclopore microfiltration membrane and a resulting pore-size distribution (Bowen et al. 1996; Bowen and Hilal 2009). There are a large number of expansions for AFM instruments allowing many other modes allowing mapping of



Atomic Force Microscopy (AFM), Fig. 1 3D image of cyclopore microfiltration membrane and pore-size distribution for same membrane obtained by AFM

electrical and electrochemical, mechanical, adhesive, frictional and magnetic properties of surfaces of interest.

As well as providing this information, the AFM probe can be used as a force sensor by moving the probe into and out of contact with the sample surface and monitoring deflection in the microcantilever arm. Through careful calibration of the system this deflection can be converted into force, directly measuring the interaction force as a function of probe tip – sample separation distance (Gibson et al. 2004). This allows the detection of DLVO, hydrophobic, hydrostatic and steric interactions, membrane stiffness, and adhesion forces. The sharp tip may be replaced by a colloidal particle, which may be functionalized to simulate any of a number of potential

membrane foulants allowing quantitative measurements of foulant rejection and attachment forces. This makes possible the direct quantification of membrane fouling properties of different materials under a range of environmental conditions and with only a relatively small sample of membrane needed.

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Atomistic Simulations Methods

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Atomistic Simulations

Atomistic simulations are theoretical and computational modeling tools for interpreting what happens at the atomic scale in solids, liquids, molecules and plasmas. Atomistic simulations,

such as phonon calculations, free-energy optimizations (molecular mechanics), molecular dynamics (MD), Monte Carlo simulations, and crystal structure prediction, are used to interpret existing experimental data and predict new phenomena and to provide a way forward where experiments are not yet possible, e.g., under extreme conditions or at atomistic size- and timescales which are difficult to detect directly (Allen and Tildesley 1989; Haile 1992; Frenkel and Smit 2002; Leach 2001; Brenner 2000; Allen 2004; Tocci and Pullumbi 2011).

Molecular modeling is primarily a tool for calculating the energy of a given molecular structure, and the goal is to understand and model the motion of each atom in the material.

Different levels of atomistic simulations exist, ranging from quantum mechanical models to statistical methods. This means solving numerically the classical or quantum mechanical microscopic equations for the motion of interacting atoms or even deeper – electrons and nuclei.

Quantum mechanical (QM) or *ab initio* methods describe matter at the electronic level, considering the fundamental particles, electrons and protons. The equation from which molecular properties can be derived is the Schrodinger equation, and various approximations must be introduced in order to extend the utility of the method to polyatomic systems.

Atomistic methods are used to compute molecular properties, which do not depend on electronic effects; the whole atom is modeled just as a soft sphere and obeys the laws of statistical mechanics. Atomistic simulation utilizes analytic potential energy expressions (sometimes referred to as empirical or classical potentials) to describe the systems.

The analytic potential energy functions are simplified mathematical expressions that attempt to model interatomic forces arising from the quantum mechanical interaction of electrons and nuclei. Their use is dictated by the need to model systems with sizes and/or timescales that exceed available computing resources, required for quantum calculations, which give no account of the complex electronic structure of atoms.

Forces between atoms are derived from empirical interatomic potentials that are obtained from fitting material properties (e.g., lattice constant, elastic constants, vacancy formation energy, etc.) from experimental data or QM calculations. They may depend on the distance between atoms, angles between bonds, angles between planes, etc.

The general form of the total potential of the N -atom system describes types of interactions, bonded and non-bonded, and can be written as:

$$V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum V_1(\vec{r}_i) + \sum_{i,j>i} V_2(\vec{r}_i, \vec{r}_j) + \sum_{i,j>i, k>j} V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

The part of the potential energy V representing bonding interactions will include terms of the following kind:

$$\begin{aligned} V_{\text{intramolecular}} = & \frac{1}{2} \sum_{\text{bonds}} K_{ij1}^r (r_{ij} - r_{eq})^2 \\ & + \frac{1}{2} \sum_{\substack{\text{bend} \\ \text{angles}}} K_{ijk}^\theta (\theta_{ijk} - \theta_{eq})^2 \\ & + \frac{1}{2} \sum_{\substack{\text{torsion} \\ \text{angles}}} \sum_m K_{ijkl}^{\phi,m} (1 + \cos(m\phi_{ijkl} - \gamma_m)) \end{aligned}$$

The “bonds” typically involve the separation $r_{ij} = |\vec{r}_i - \vec{r}_j|$ between adjacent pairs of atoms in a molecular framework, and a harmonic form with specified equilibrium separation has been used, although this is not the only possible type. The “bend angles” θ_{ijk} are between successive bond vectors such as $\vec{r}_i - \vec{r}_j$ and $\vec{r}_j - \vec{r}_k$ and involve three atom coordinates. Usually this bending term is quadratic in the angular displacement from the equilibrium value, although periodic functions are also used. The “torsion angles” ϕ_{ijkl} are defined in terms of three connected bonds; hence four atomic coordinates are used.

The part of the potential energy V representing non-bonded interactions between atoms is

traditionally split into one-body, two-body, three-body terms:

$$\begin{aligned} V_{\text{non-bonded}}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \\ = \sum_i v(\vec{r}_i) + \sum_i \sum_{j>i} w(\vec{r}_i, \vec{r}_j) + \dots \end{aligned}$$

The $v(\vec{r}_i)$ term represents an externally applied potential field and describes external force fields (e.g., gravitational field) and external constraining fields (e.g., the “wall function” for particles in a chamber). The pair potential $w(\vec{r}_i, \vec{r}_j) = w(r_{ij})$ neglect three-body (and higher order) interactions.

The Lennard-Jones potential is the most commonly used form:

$$w^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where σ is the diameter and ϵ is the depth of the potential energy well. If electrostatic charges are present, the appropriate Coulomb potentials are added:

$$w^{\text{Coulomb}}(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0 r}$$

where Q_1, Q_2 are the charges and ϵ_0 the permittivity of the free space.

To be effective, an analytic potential energy function must possess the following critical properties:

Flexibility: A potential energy function must be sufficiently flexible that it accommodates as wide a range as possible of fitting data.

Accuracy: A potential should be able to accurately reproduce properties of interest as closely as possible.

Transferability: A potential function should be able to study a variety of properties for which it was not fit.

Computational efficiency: Evaluation of the function should be relatively efficient depending on quantities such as system sizes and timescales of interest, as well as available computing resources.

The major methods are molecular mechanics (MM), molecular dynamics (MD), Monte Carlo (MC), and additionally, there is a whole range of hybrid techniques which combine features from both MD and MC methods.

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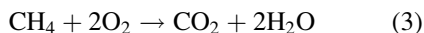
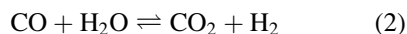
Autothermal Reforming

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Autothermal reforming or oxidative steam reforming is a combination of conventional

steam reforming of the fuel (endothermic reaction) with the partial oxidation of a small amount of the fuel (exothermic reaction) in order to achieve an autothermal reaction that proceeds without external input of energy (Chang et al. 2010; Tiemersma et al. 2012).

The most studied autothermal reforming is the conversion of methane to hydrogen (Gallucci et al. 2009). The overall chemical reactions taking place in the autothermal reforming of methane include steam reforming (Eq. 1), water gas shift (Eq. 2), and total oxidation (Eq. 3). The energy generated by the oxidation reaction and WGS is used for the SMR:



This reaction system can be carried out efficiently in a membrane reactor as the extraction of hydrogen during the reaction shifts the equilibrium reactions toward completion at moderate temperatures, and thus the extent of oxidation reaction to achieve autothermal reforming is moderate.

One of the problems of autothermal reforming carried out in membrane reactors is the mismatch between the oxidation reaction rate and the reforming reaction rate. The oxidation is often much faster than the reforming, and for this reason in packed bed membrane reactors, a high-temperature region is obtained at the beginning of the bed followed by a low-temperature region at the end of the bed. This could cause problems to the membranes that could be damaged by high temperatures while not working properly (low flux – see Richardson equation) at lower temperatures (Tiemersma et al. 2006; Gallucci et al. 2010).

To circumvent these problems, fluidized bed membrane reactors are often proposed for this kind of reaction system, as the solid circulation inside the reactor allows a virtually isothermal condition even in case of highly exothermic reactions.

Examples of autothermal reforming (ATR) (or oxidative steam reforming) reactions also include the ATR of ethanol and methanol or the ATR of naphtha (Lin et al. 2010; Tosti et al. 2010; Moreno and Wilhite 2009). All these reactions have been successfully tested in membrane reactors for pure hydrogen production.

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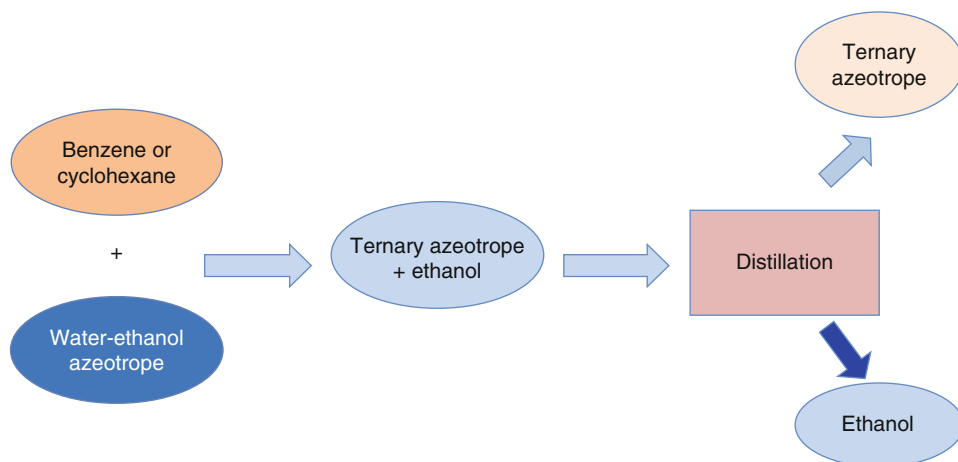
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Azeotropic Distillation

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Azeotropic distillation is a particular type of distillation by which it is possible to separate azeotropes (Perry and Green 1984). Azeotropes are mixtures of two or more substances that boil together at a constant temperature. It is, therefore, impossible to separate them directly by distillation, because a distillate of the same composition of the liquid feed is produced. Azeotropic distillation is based on the addition of a compound that acts on the volatility of the substances contained into the azeotrope, so that a new azeotrope, made of the substances present in the starting azeotrope and the added compound, is formed. The new azeotrope can be, then, removed by distillation, and a residual highly rich in one of the substances is obtained. A typical example is the distillation of mixtures of water-ethanol. By classic distillation, the distillate contains 95 % of alcohol (pure boiling temperature, 78.4 °C) and 5 % of water (pure boiling temperature, 100 °C), and no further increments in ethanol purity can be reached, because this mixture boils, as a unique compound, at 78.17 °C. However, if benzene or cyclohexane is added to the mixture, a ternary azeotrope is formed that incorporates all the water and has a lower boiling point than ethanol. Therefore, if the distillation is now carried out, the new azeotrope will be recovered as distillate, while practically pure ethanol is produced as residue (see Fig. 1). Besides



A

Azeotropic Distillation, Fig. 1 Azeotropic distillation of water-ethanol

azeotropic distillation, other methods can be also employed for the separation of azeotropes and, in particular, membrane operations like pervaporation and membrane distillation.

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B

β -Lactoglobulin and α -Lactalbumin Separation

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β -Lactoglobulin and α -lactalbumin are the two dominant proteins in whey (see Table 1). Although whey protein concentrates are used as food additives in the production of a variety of dairy products, meats, and beverages, the unique nutritional, therapeutic, and functional characteristics of the individual whey proteins are largely unrealized in these whey products. There has thus been considerable commercial interest in the separation of β -lactoglobulin and α -lactalbumin to take advantage of their functional and biological properties. α -Lactalbumin is attractive as a nutraceutical because of its high tryptophan content (Cayot and Lorient 1997). α -Lactalbumin also provides enhanced whippability in meringue-like formulations and may have potential as a contraceptive agent. β -Lactoglobulin is an effective foam

stabilizer and can be used in the production of confections (Cayot and Lorient 1997).

There are two types of membrane systems that have been explored for the separation of β -lactoglobulin and α -lactalbumin: ultrafiltration and membrane adsorbers (also referred to as membrane chromatography). Cheang and Zydney (2003) demonstrated that β -lactoglobulin and α -lactalbumin could be separated using commercial ultrafiltration membranes by adjusting the solution pH and ionic strength to enhance the selectivity. These results were subsequently extended to purify β -lactoglobulin and α -lactalbumin from a whey protein isolate using a two-stage ultrafiltration process (Cheang and Zydney 2004).

Membrane chromatography is of potential interest for the separation of β -lactoglobulin and α -lactalbumin due to the high flow rates that can be achieved in these systems. For example, Saufi and Fee (2011) examined the use of a mixed mode membrane chromatography system containing both cation and anion exchange sites for the fractionation of whey proteins. β -Lactoglobulin was preferentially bound to the membrane, with the α -lactalbumin collected in the flow through.

β -Lactoglobulin and Alpha-Lactalbumin Separation, Table 1 Physical characteristics of major whey proteins (From Zydney 1998)

Protein	Concentration (g/L)	Molecular weight (g/mol)	Isoelectric pH
β -Lactoglobulin	2.7	18,362	5.2
α -Lactalbumin	1.2	14,147	4.5–4.8
Immunoglobulins	0.65	150,000–1,000,000	5.5–8.3
Bovine serum albumin	0.4	69,000	4.7–4.9
Lactoferrin	0.1	78,000	9.0
Lactoperoxidase	0.02	89,000	9.5
Glycomacropeptide		7	

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Backwashing

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Backwashing of a membrane refers to the reversal of flow through a membrane system in comparison to the normal flow direction required for permeate production. The purpose of backwashing is to assist with removing or loosening foulants from the membrane surface and within the membrane pores to control membrane fouling. It is a fundamental membrane operational step to control the rate of transmembrane pressure (TMP) increase over time. Backwashing is utilized with low

pressure membrane systems, i.e., microfiltration and ultrafiltration, while high pressure membrane systems, i.e., nanofiltration and reverse osmosis, do not employ backwashing to control fouling. Backwashing is most commonly initiated on a timed cycle; however, it may also be initiated on a transmembrane pressure set point or a volume filtered set point (AWWA 2013). Backwashing is performed in stages through a membrane plant in order to ensure that water is being produced at all times; in other words, there is rotation through which individual membrane units will be backwashed, while the majority, at any given time, are still maintained in operation. When backwashing is no longer considered effective at controlling membrane fouling, as indicated by a set point loss in flux, permeate production, or high TMP value, the membrane system will undergo chemical cleaning. Additionally, a chemically enhanced backwash (CEB) may be put in place before a membrane unit is taken off-line for a full chemical clean. In the event of a CEB, an oxidant, such as chlorine, and acids or bases, such as citric acid or sodium hydroxide, are added to the backwash water to assist in the removal of foulants from the membrane pores and membrane surface.

Backwashing has been found to be helpful in removing cake layer fouling that is particulate in nature. However, research has shown that backwashing alone does not remove the majority of the cake layer fouling but instead mainly increases its porosity, effectively loosening the cake layer against the membrane surface (Ye et al. 2011). Therefore, it is important to include an air scour or cross-flow velocity step with backwashing to effectively decrease the size

and thickness of the cake layer foulants on the membrane surface (Remize et al. 2010). However, it is important to keep in mind that pore blocking results in a faster deterioration of the membrane flux and is more likely to lead to irreversible fouling than cake layer fouling. The cake layer itself can prevent pore blocking by acting like a prefilter for the membrane surface. Thus, if too much of the cake layer is removed, the membrane system will have a faster development of pore blocking over several cycles of backwashing. As such it is important to configure an optimized backwash procedure with associated air scour or cross-flow velocity step for a particular membrane and water type. When optimizing a system, it is important to note that research has found that backwash duration and backwash flux at low rates, equal to or less than the permeate flux, are not likely to have an impact on fouling rate in low fouling systems, although backwash duration was found to have an optimum value associated with net permeate production (Akhondi et al. 2014). Other research has shown that too high of a backwash flux may actually exacerbate fouling by potentially removing too much of the cake layer and resulting in more irreversible pore fouling occurring (Wu et al. 2008). Given that backwashing has been shown to clearly assist in controlling fouling, it is important for all membrane plants to monitor the effectiveness of their backwash procedures on a regular basis with consideration for changes in water quality over different seasons.

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Backwashing Frequency

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Optimization of backwash frequency is an important consideration in terms of membrane operation as it uses produced water for the backwash cycle; therefore, the more frequent the backwash, the lower the efficiency of the membrane system overall in terms of produced water. In addition to the backwash frequency, which is generally every 30–90 min, consideration should also be applied for backwash duration and backwash flux. Backwash duration is how long a membrane system is backwashed and is typically between 1 and 3 min. In some cases, backpulsing may also be used, and this term refers to short burst cycles for reversing the flow through the membrane that generally last between 0.5 and 5 s. Backwash flux is the fluid flow rate through the membrane, and it is generally equal to the initial operating permeate flux of the membrane system, although it may be higher. Backwash frequency is linked to the operating membrane flux, with a lower flux resulting in a lower required backwash frequency, while a higher flux tends to require a higher backwash frequency (Wang et al. 2008; Raffin et al. 2011).

Backwashing is often considered to control reversible fouling; however, it is also tied to the control of irreversible fouling as well. Research has demonstrated, for instance, that while backwash frequency may not appear to impact on the rate of reversible fouling, it can influence the rate of irreversible fouling. Specifically, longer periods between backwashes (i.e., 60 min vs. 30 min)

resulted in an increase in the irreversible fouling rate (Raffin et al. 2012). The importance of this information is that higher irreversible fouling rates result in higher frequencies of chemical cleaning for a membrane system, which has both an adverse impact on water production and the economics of running a membrane system. Of course, consideration must be taken for the loss of system productivity when increasing the frequency of backwashing as well. As backwash frequency increases, the membrane productivity is concomitantly decreasing; backwashing can result in upwards of a 10 % loss in membrane productivity. It is, therefore, important to weigh out the benefits and losses associated with increasing backwashing frequency and losing productivity versus decreasing the backwash frequency and potentially increasing the required chemical cleaning of the membrane system.

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Bacteria and Spore Removal

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Bacteria can be of great influence on many processes, be it in, for example, food, pharma, fermentation, or water production. Obviously, bacteria (and their spores) can be removed by heat treatment or addition of specific components that inhibit their growth or even kill them, but the

downside of this is that the product properties will be influenced and this is mostly undesirable. In this respect, membrane microfiltration could be an interesting alternative when used for cold sterilization. If the bacterial count is not too high and other components are sufficiently smaller, the removal of bacteria and spores can rather easily be carried out using dead-end microfiltration.

When the size of bacteria and other components overlap, this separation is far from straightforward. An illustrative example can be found in dairy separation, in which cold sterilization of “milk” has been reported. The components that are most important for this separation are the milk fat globules (cream; typical sizes from 0.1 to 15 μm), bacteria (0.5–5 μm), and casein micelles (20–300 nm). Since cream and bacteria overlap in size, the cream is first removed by centrifugation. The resulting skim milk receives the cold sterilization treatment. Various researchers have investigated how far the bacterial count could be reduced as listed in Table 1.

From the table, it is clear that a variety of membranes and process conditions have been used, ranging from very high to low cross-flow velocities, and application of a uniform transmembrane pressure or frequent back pulsing. These conditions are clearly aiming at processing under very different conditions, where frequent back pulsing will control the amount of deposited material, the uniform transmembrane pressure concept aims at stable filtration conditions along the length of the membrane. All approaches have shown interesting results; the log reductions that can be achieved are around 4 (10,000-fold reduction), although it should be noted that these values are not as high as obtained after regular heat treatment.

The highest log reduction (6.6, which is higher than for regular pasteurization) was claimed for microsieves, which are silicon plates with very uniform pores prepared by laser interference lithography (Van Rijn and Elwenspoek 1995). Although the bacterial reduction was measured for dead-end filtration using a 0.5 μm microsieve and SMUF (simulated ultrafiltrate) spiked with *Bacillus subtilis*, it is expected that the high log

Bacteria and Spore Removal, Table 1 Comparison of cold sterilization results from various sources

Membrane type and flux	Process conditions cross-flow/pressure, UTP, back pulsing	Log reduction	Source
Ceramic 1.4 μm; 1.4•10 ⁻⁴ m/s	50 kPa, 7.2 m/s UTP, skim milk	Above 3.5	Saboya and Maubois 2000
Reversed asymmetric 0.87 μm; 1.4•10 ⁻⁴ m/s	0.5–1 m/s; back pulsing frequency 0.2–1 s ⁻¹ , skim milk	Between 4 and 5	Guerra et al. 1997
Microsieve 0.5 μm	Dead-end filtration of spiked SMUF	6.6	Van Rijn and Kromkamp 2001
Bactocatch: ceramic membranes	6–8 m/s, skim milk, UTP		Holm et al. 1989

count reduction is a result of its narrow pore size distribution of the microsieve.

In case of the uniform transmembrane pressure concept, reduction of bacteria and spores by microfiltration is carried out near the critical pressure, at which the amount of particles that is carried toward that membrane by permeate is counterbalanced by the amount of particles diffusing away from the membrane to the feed solution. We expect that this can be even taken one step further, as indicated in the work of van Dinther et al. (2011), in which particles that size-wise correspond to milk fat globules and bacteria were reported to be separated by fluid skimming and lift effects. For this to occur, first a nonporous channel is used to induce particle migration after which in a porous area the small particles that are situated close to the wall can specifically be removed. This process has not been demonstrated at large scale, but it holds great promise since it would allow for direct separation of bacteria from full milk without the need of centrifugation. Besides, the separation is no longer determined by the pore size of the membrane; metal sieves from SPG Veco with uniform pores of around 20 μm were used, but by the process conditions that determine which part of the feed is removed.

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Bacterial Adhesion

► Bacterial Biofilm Formation

Bacterial Biofilm

► Bacterial Biofilm Formation

Bacterial Biofilm Formation

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Synonyms

Bacterial biofilm; Bacterial adhesion; Biofouling

Biofilms were observed as early as 1674, when Antonie van Leeuwenhoek used his primitive but effective microscope to describe aggregates of “animalcules” that he scraped from human tooth surface (Costerton 1999). Since then, more accurate descriptions of biofilms are made. Bacteria generally exist in one of two types of population: planktonic, freely existing in bulk solution, and sessile, as a unit attached to a surface or within the confines of a biofilm (Garrett et al. 2008).

Biofilm is a result of many complicated steps. It includes the formation of a conditioning film on a material's surface, the movement of bacteria, an attachment process, the growth on material surfaces, and the breakdown finally. For bacteria, the advantages of biofilm formation are numerous. These advantages include: protection from antibiotics (Godberg 2002), disinfectants (Peng et al. 2002), and dynamic environments (Chen et al. 1998).

Over the past few decades, biofilm growth has been observed in many industrial and domestic domains. Many industries suffer the ill effects of biofilm growth of one type or another, which can result in heavy costs in cleaning and maintenance. Biofilms occurring in membrane systems may cause severe loss performance and the use of costly cleaning procedures to maintain output and quality. The fouling is often so severe that acceptable operation cannot be maintained and membrane replacements are needed. It is necessary to understand the biofilm formation mechanism with the aim to propose a solution to contrast this fouling.

Bacteria are capable of colonizing almost any surface and have been found at extreme conditions such as temperatures from -12°C to 110°C and pH values between 0.5 and 13.

Biofilm growth occurs by physical, chemical, and biological processes. Fletcher described the accumulation of microorganisms on a collecting surface as a process of three stages: (i) adsorption, or the accumulation of an organism on a collector surface, i.e., substrate (deposition); (ii) attachment, or the consolidation of the interface between an organism and a collector, often involving the formation of polymer bridges between the organism and collector; and (iii) colonization, or growth and division of organisms on

the collector's surface. Although useful as a snapshot of biofilm growth, this type of profile is limited when considering the intimate processes of cell–substrate/cell–cell interaction. Characklis and Marshal later described an eight-step process which included the formation of an initial conditioning layer, reversible and irreversible adhesion of bacteria, and the eventual detachment of cells from a mature biofilm for subsequent colonization.

Anything that may be present within the bulk fluid can through gravitational force or movement of flow settle onto a substrate and become part of a conditioning layer. This layer modifies substrata facilitating accessibility to bacteria. Surface charge, potential, and tensions can be altered favorably by the interactions between the conditioning layer and substrate. The substrate provides anchorage and nutrients augmenting growth of the bacterial community.

Initially, planktonic microbial cells are transported from bulk liquid to the conditioned surface either by physical forces or by bacterial appendages such as flagella. The reversible adsorption of a fraction of the cells reaching the surface normally occurs. Local environmental variables which contribute to bacterial adhesion are factors such as available energy, surface functionality, bacterial orientation, temperature, and pressure conditions. If repulsive forces are greater than the attractive forces, the bacteria will detach from the surface. The probability of this phenomenon occurs is higher before the formation of the conditioning layer. The activation energy for desorption of bacteria is low and so it is likely to occur, underlining the weakness of the bonds. Physical forces associated to bacterial adhesion include the van der Waals forces, steric interactions, and electrostatic (double layer) interaction, collectively known as the DVLO (Derjaguin, Verwey, Landau, and Overbeek) forces, which originally described the interaction of a colloidal particle with a surface (Rutter and Vincent 1980). According to this theory, the total interaction between a surface and a particle is the summation of their van der Waals and Coulomb interactions. Since the van der Waals attractive force is dominant in the vicinity of a surface, particles adhere

irreversibly because they cannot separate from the surface by Brownian motion. In contrast, the Coulomb interaction becomes dominant at a distance away from the surface because the van der Waals force decreases sharply with distance. Other interactions that DVLO theory takes into consideration are hydrophobic–hydrophilic and osmotic (Chang and Chang 2002) and have also been described in terms of thermodynamic interaction (Gallardo-Moreno et al. 2002).

In real time, a number of the reversibly adsorbed cells remain immobilized and become irreversibly adsorbed. It has been argued that the physical appendages of bacteria (flagella, fimbriae, and pili) overcome the physical repulsive forces of the electrical double layer (De Weger 1987). Subsequently, the appendages make contact with the bulk lattice of the conditioning layer stimulating chemical reactions such as oxidation and hydration and consolidating the bacteria–surface bond. Some evidence has shown that microbial adhesion strongly depends on the hydrophobic–hydrophilic properties of interacting surfaces (Liu et al. 2004).

As the stationary cells divide (binary division), daughter cells spread outward and upward from the attachment point to form clusters. Typically, such interactions and growth within the developing biofilm form into a mushroom-like structure. This structure is believed to allow the passage of nutrients to bacteria deep within a biofilm. After an initial stage, a rapid increase in population is observed, otherwise described as the exponential growth phase. This depends on the nature of the environment, both physically and chemically. The rapid growth occurs at the expense of the surrounding nutrients from the bulk fluid and the substrate. At this stage the physical and chemical contribution to the initial attachment ends and the biological processes begin to dominate. Excretion of polysaccharide intercellular adhesin (PIA) polymers and the presence of divalent cations interact to form stronger bonding between cells (Dunne 2002).

Differential gene expression between the two bacterial states (planktonic/sessile) is in part associated to the adhesive needs of the population. For example, the production of surface appendages is

inhibited in sessile species as motility is restricted and no longer necessary. Simultaneously, expression of a number of genes for the production of cell surface proteins and excretion products increases. Surface proteins (porins), such as Opr C and Opr E, allow the transport of extracellular products into the cell and excretion materials out of the cell, e.g., polysaccharides (Hancock et al. 1990). The structure of many Gram-negative bacterial polysaccharides is relatively simple, comprising either homopolysaccharides or heteropolysaccharides (Sutherland 2001). These molecules impart mechanical stability and are pivotal to biofilm adhesion and cohesion and evasion from harsh dynamic environmental conditions. They consolidate the biofilm structure. Hall-Stoodley and Stoodley identified the differences in gene expression of planktonic and sessile cells, and as many as 57 biofilm-associated proteins were not found in the planktonic profile.

The stationary phase of growth describes a phase where the rate of cell division equals the rate of cell death. At high cell concentration, a series of cell signaling mechanisms are employed by the biofilm, and this is collectively termed quorum sensing (Bassler 1999). Quorum sensing describes a process where a number of autoinducers (chemical and peptide signals in high concentrations, e.g., homoserine lactones) are used to stimulate genetic expression of both mechanical and enzymatic processors of alginates, which form a fundamental part of the extracellular matrix. The death phase sees the breakdown of the biofilm. Enzymes are produced by the community itself which break down polysaccharides holding the biofilm together, actively releasing surface bacteria for colonization of fresh substrates. Alginate lyase produced by *Pseudomonas fluorescens* and *Pseudomonas aeruginosa*, N-acetyl-heparosan lyase by *Escherichia coli*, and hyaluronidase by *Streptococcus equi* are examples of the enzymes used in the breakdown of the biofilm matrix (Sutherland 1999). Simultaneously, the operons coding for flagella proteins are upregulated so that the organisms have the apparatus for motility and the genes coding for a number of porins are downregulated, thus

completing a genetic cycle for biofilm adhesion and cohesion.

Changes in pH can have a marked effect on bacterial growth and as such are frequently exploited in the production of detergents and disinfectants used to kill bacteria. Bacteria possess membrane-bound proton pumps which extrude protons from the cytoplasm to generate a transmembrane electrochemical gradient (Rowland 2003), i.e., the proton motive force. The passive influx of protons in response to the proton motive force can be a problem for cells attempting to regulate their cytoplasmic pH (Booth 1985). Large variations in external pH can overwhelm such mechanisms and have a biocidal effect on the microorganisms. Bacteria respond to changes in internal and external pH by adjusting the activity and synthesis of proteins associated with many different cellular processes (Olsen 1993). Studies have shown that a gradual increase in acidity increases the chances of cell survival in comparison to a sudden increase by rapid addition of HCl (Li 2001). This suggests that bacteria contain mechanisms in place which allow the bacterial population to adapt to small environmental changes in pH. However, there are cellular processes which do not adapt to pH fluctuations so easily. One such process is the excretion of exopolymeric substances (polysaccharides). Optimum pH for polysaccharide production depends on the individual species, but it is around pH 7 for most bacteria.

Both mixed species and pure culture biofilms behave like viscoelastic fluids. Biofilms exhibit both irreversible viscous deformation and reversible elastic response and recoil (Ohashi and Harada 2004). Extracellular polymeric substances like alginate, xanthan, and gellan gum aggregate due to hydrogen bonding to form highly hydrated viscoelastic gels (Stoodley et al. 1999). The presence of acetylated uronic acids in the bacterial alginate of *P. aeruginosa* biofilms increases its hydration capacity. These properties provide the biofilm with mechanical stability (Stoodley et al. 2002).

The matrix formed by EPS responds to stress by exhibiting (i) elastic tension due to a combination of polymeric entanglement, entropic, and

weak hydrogen bonding forces; (ii) viscous damping due to polymeric friction and hydrogen bond breakage; and (iii) alignment of the polymers in the shear direction (Klapper et al. 2002). Such properties change with increased temperature. Increasing the temperature of polysaccharides produces a gel-like substance which gradually increases in strength until a critical point is reached. At the critical point the gel forms a solution (Villain-Simonnet et al. 2000). Such behavior affects the viscosity of the polysaccharides which can affect biofilm adherence. The optimum temperature for a microorganism is associated with an increase in nutrient intake resulting in a rapid formation of biofilm (Stepanovic et al. 2003). Enzymes are responsible of nutrient metabolism; then the formation of a biofilm is dependent on the presence and reaction rates of enzymes. Temperature influences the reaction rate of enzymes having an impact on the development of the cells. Optimum temperatures result in the healthy growth of bacterial populations. Temperatures away from the optimum negatively influence bacterial enzyme reaction rates, and a reduction of bacterial growth efficiency occurs. Fletcher reported the effect of temperature on attachment of stationary phase cells. Findings showed that a decrease in temperature reduced the adhesive properties of a marine *Pseudomonad*. It is believed that the effect was due to a decrease in the bacterial surface polymer at lower temperatures as well as effects such as reduced surface area. However, Herald and Zottola observed that the presence of bacterial surface appendages was dependent on temperature. At 35 °C cells were shown to have a single flagellum, while at 21 °C they had two to three flagella, and at 10 °C, cells exhibited several flagella. This may suggest that the initial interaction between the bacteria and substrate may increase with a lowering of temperature, increasing the likelihood of adhesion. Perhaps the more uniform properties of polysaccharides at lower temperatures increase the possibility of biofilm adhesion, because many microbial polysaccharides undergo transition from an ordered state at lower temperatures and in the presence of ions to a disordered

state at elevated temperature under low ionic environments (Nisbet et al. 1984).

Although there is plenty of information describing the effect of temperature on bacterial growth in culture, the effect of temperature on the removal of adhered microorganisms is not so well documented. The reports available describe fairly radical effects of temperature on adhered bacteria. Marion-Ferey et al. observed the effect of high temperatures (80–90 °C) on the removal of biofilms. It was discovered that these temperatures were not effective for biofilm removal due to “baking effects” at high temperature, apparently increasing the adherent nature of the biofilm to the surface.

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BAL

► Bioartificial Liver

Barium Sulfate (BaSO₄), Fouling due to

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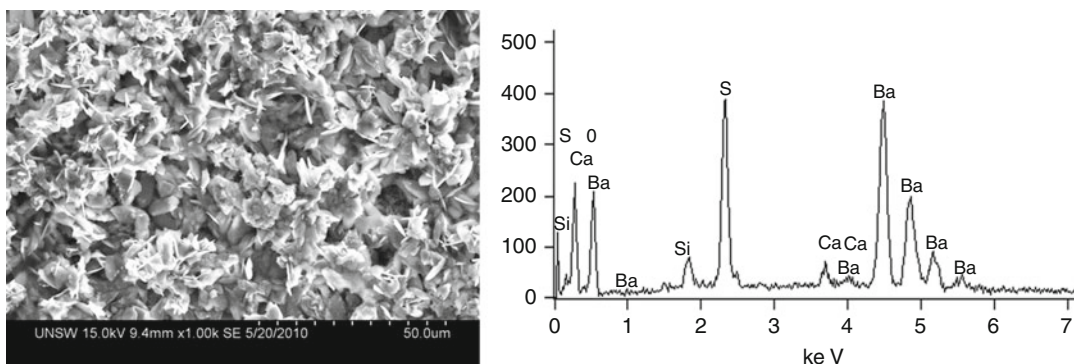
Barium sulfate or barite, BaSO₄ is a nonalkaline scale, particularly problematic in membrane systems due to its extremely low solubility, 10⁻⁵ mol/l (equivalent to 2.33 mg/l) in pure water. Also, this scale is extremely difficult to remove and clean from membrane surfaces if not detected at an early stage and is allowed to age into a hard adherent layer. BaSO₄ could originate from various sources. In the offshore oil industry for example, seawater (containing high level of sulfate) is

injected into reservoirs, and the resulting mixture generally features stable supersaturated BaSO₄, ready to precipitate. While alkaline scales can be controlled by altering the feed pH prior to filtration, sulfate scales are insensitive to pH and therefore cannot be controlled by acid addition. BaSO₄ scales are usually needle shape crystals which can easily damage the active layer of the membrane, resulting in loss of integrity (Fig. 1).

Du Pont method is widely applied as prediction method for BaSO₄ scale in RO systems using the salt solubility at 25 °C and the solubility product, K_c (Boerlage 2001). The K_c expresses the dynamic equilibrium between the scalant crystal ions in solution and the crystal solid phase, for example, the K_c for BaSO₄ is expressed as:

$$K_c = [Ba^{2+}][SO_4^{2-}] \quad (\text{at equilibrium})$$

K_c is determined graphically as a function of ionic strength for the desired recovery (Boerlage et al. 1999). The relationship between K_c and ionic strength is derived from data on the effect of individual monovalent and divalent cations on barium solubility. When the scalant concentration product exceeds K_c, the solution is supersaturated and scaling may occur. Du Pont recommends a recovery such that the scalant concentration product is 20 % below the K_c to prevent scaling. This ensures a safety factor for concentration polarization which may occur at the membrane surface,



Barium Sulfate (BaSO₄), Fouling due to, Fig. 1 SEM-EDS images showing BaSO₄ scaling on RO membrane treating cooling water from power plant (Picture provided by Dr Alice Antony, The University of New South Wales, Australia)

causing a higher localized concentration than in the bulk solution (Boerlage 2001). The major limitation of this index is that it lacks background information on interactions between ionic species on saturation concentrations; as a result, it also neglects the effects of common and uncommon ions on solubility of scale forming species and the interactions between ionic species.

Addition of antiscalant is the common method to control the BaSO_4 scale formation. However, continuous monitoring of the RO performances through conventional techniques lacks the sensitivity to detect the subtle changes occurring across the membrane, and in particular, early deposition of BaSO_4 . This lack of detailed and timely assessment of the fouling state can result in delay in applying the necessary cleaning strategies, whose efficiency is limited for fully developed BaSO_4 scaling layers, known to be particularly resistant to conventional cleaning methods. When BaSO_4 scaling is observed during autopsy analysis, crown ethers and concentrated sulphuric acid are generally recommended as cleaning agents, causing partial membrane hydrolysis (Van der Leeden 1991). Alkaline chelants have also been reported to be efficient cleaning agents (Chesters 2009).

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Basic Electrochemical Relations in Membrane Processes: Electron Conductivity, Ion Conductivity, Ohm's Law, and Coulomb's Law

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In certain membrane processes, charged components such as salt solutions are separated by neutral membranes or membrane carrying fixed positive or negative charges using an electrical potential as driving force. The behavior of ions in solution and in a membrane is rather different from that of uncharged components because of the strong interaction of electrical charges with each other and their surrounding. Therefore some fundamental electrochemical relations shall be briefly reviewed.

Electron and Ion Conductivity and Ohm's Law

The transport of electric charges, i.e., an electric current, can be achieved by two characteristic modes (Kortüm 1957), i.e., by:

- Transport of electrons through solid material such as metals
- Transport of ions through liquids such as electrolyte solutions

The conductivity of electrons, i.e., metal conductors, is generally three to five orders of magnitude higher than the conductivity of electrolyte solutions. Furthermore, the conductivity of metals is decreasing with increasing temperature, while the conductivity of electrolyte solutions is increasing with the temperature. The most important difference between electron and ion conductivity,

however, is the fact that ion conductivity is always coupled with a transport of mass, while due to the very small mass of an electron virtually no mass is transported in an electron conductor. In spite of the basic difference in the transport mode between electron and ion conductivity, the electrical current can be described in both cases by the same mathematical relation which states that the electrical current is proportional to the electrical potential driving force. This relation is referred to as Ohm's law which is given by

$$\varphi = RI \quad (1)$$

Here φ is the electrical potential between two electron sources, e.g., between two electrodes in an electrolyte solution expressed in Volt, I is the electrical current between the electron sources expressed in ampere, and R is the electrical resistance expressed in ohm.

The resistance R is a function of the specific resistance of the material, the distance between the electron sources, and the cross-section area of the material through which the electric current passes. It is given by

$$R = \rho \frac{l}{q} \quad (2)$$

Here R is the overall resistance, ρ is the specific resistance, l is the length, and q is the cross-section area of the conducting material.

The reversal of the resistance and of the specific resistance, respectively, is the conductivity and the specific conductivity and thus is

$$S = \frac{1}{R} \text{ and } \kappa = \frac{1}{\rho} \quad (3)$$

Here S is the conductivity and κ is the specific conductivity.

The conductivity of electrolyte solutions depends on the concentration and the valence of the ions in the solution. It is expressed as the equivalent conductivity or molar conductivity (Harned and Owen 1958). For a solution of a single electrolyte, the equivalent conductivity is given by

$$\Lambda_{eq} = \frac{\kappa}{C(z_a v_a + z_c v_c)} \quad (4)$$

Here Λ_{eq} is the equivalent conductivity of an electrolyte; C is the molar concentration of the electrolyte in the solution; z_a and z_c are the charge numbers of the anion and cation, respectively; and v_a and v_c are the stoichiometric coefficients of the anion and cation, respectively.

The stoichiometric coefficient gives the number of anions and cations in a mole electrolyte, and the valence gives the number of charges related to an ion. For example, for NaCl v_c and v_a are identical and 1 and also z_a and z_c are 1. However, for MgCl_2 v_c is 1 and v_a is 2, and z_c is 2 and z_a is 1.

The equivalent conductivity can be expressed as the sum of the contributions from its individual ions. Thus

$$\Lambda_{eq} = \lambda_a + \lambda_c \quad (5)$$

Here Λ_{eq} is the equivalent conductivity and λ_a and λ_c are the equivalent conductivities of anion and cation, respectively.

The electrical current passing through an electrolyte solution under the driving force of an electrical potential gradient is proportional to the concentration of the ions in the solution, the stoichiometric coefficients for cat- and anions, and the number of electrical charges carried by one ion, i.e., its valence and the ion mobility in the electrolyte solution. The number of electrical charges carried by all ions of an electrolyte under the driving force of an electrical potential gradient through a certain area A is given by

$$J_e = \sum_i z_i u_i v_i C e N_A \Delta\varphi = \sum_i z_i F J_i \quad (6)$$

Here J_e is the flux of electrical charges and J_i that of the individual ions; z , u , and v are the charge number, the ion mobility, and the stoichiometric coefficient, respectively; C is the concentration of the electrolyte; e is the charge of an electron, N_A the Avogadro number, φ an electrical potential, and the subscript i refers to the ions in the solution; and F is the Faraday constant.

The ion mobility u has the dimension $\text{m}^2\text{s}^{-1}\text{V}^{-1}$. The charge of an electron is $e = 1.6019 \times 10^{-19}$ C, and the Avogadro number is $N_A = 6.0232 \times 10^{23}$ molecules per mol or in this case electrical charges per mole. The product of e and N_A is called the Faraday constant which is $F = 96,485$ C eq^{-1} (Atkins 1990).

The flux of electrical charges represents an electrical current, which is for a solution of a single electrolyte according to Ohm's law given by

$$I = \frac{U}{R} = \sum_i z_i F J_i A = \frac{\sum_i z_i u_i v_i C F A \Delta\varphi}{l} \quad (7)$$

Here I is the current, U is the applied voltage, R is the resistance, A is the area through which the current passes, $\Delta\varphi$ is the voltage difference between two points, and l is the distance between the two points.

Coulomb's Law and the Electric Field Effect on Ions in Solution

Electrical charges carried by ions interact with each other. Opposite charges attract each other and identical charges repel each other. The interaction force between two point electrical charges q_1 and q_2 in a vacuum separated by a distance r is given by

$$K = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \quad (8)$$

Here K is the interaction force between two point electrical charges, q_1 and q_2 are electrical charges, r is the distance between the two point electrical charges, and ϵ_0 is the permittivity of vacuum.

Equation 8 is referred to as Coulomb's law and the electrical charge is expressed in Coulomb.

The permittivity depends on the medium between the electrical charges. In a vacuum the permittivity is a fundamental constant denoted as ϵ_0 . It has the value 8.854×10^{-12} $[\text{C}^2 \text{J}^{-1} \text{m}^{-1}]$. If the medium is not a vacuum, the permittivity can

be expressed in terms of a relative permittivity ϵ_r which is also referred to as dielectric constant of the medium (Atkins 1990). It is given by

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (9)$$

Here ϵ , ϵ_r , and ϵ_0 are the permittivity of a medium, the relative permittivity, and the permittivity in the vacuum, respectively.

Coulomb's law describes the interaction between two point charges. In some cases it is desirable to know the force exerted by one charge q in a certain distance r to its surrounding. This force is referred to as electric field. It is given by

$$E = \frac{K}{q} \quad (10)$$

Here K is the force, E is the electric field, and q is an electrical charge.

In determining the electric field, the direction of the field must be taken into account. For a point electrical charge q , the electric field is radial symmetric (Starzak 1984; Kortüm 1957) and given by

$$E = \frac{q}{4\pi\epsilon r^2} \quad (11)$$

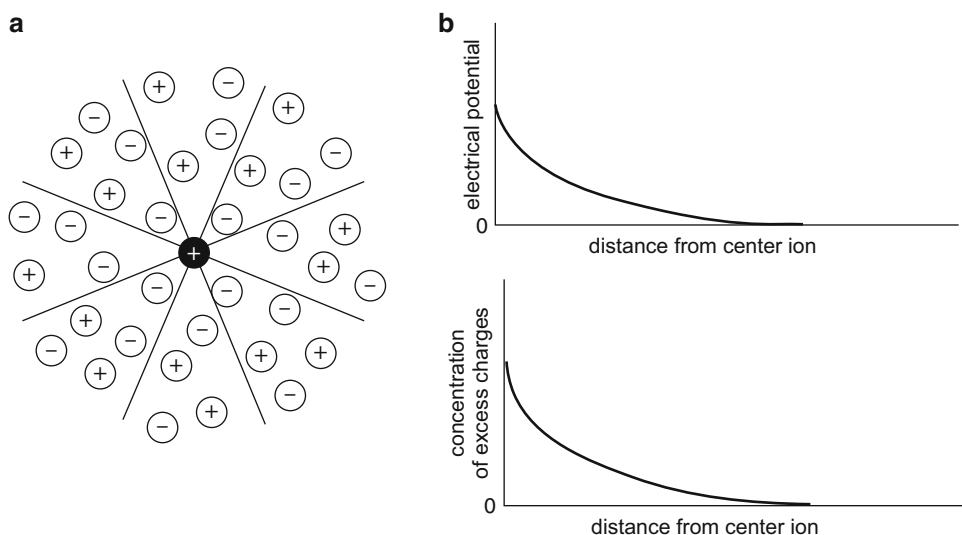
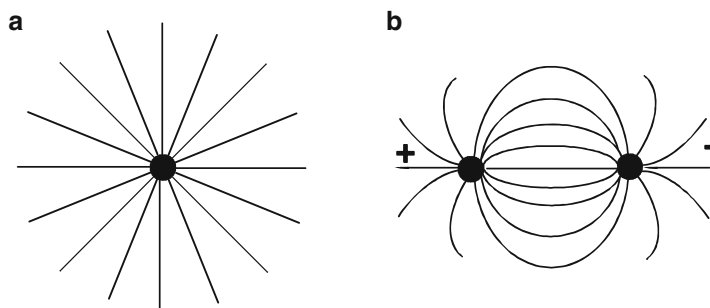
Here E is the electric field around a point electric charge q , r is the distance from the electrical charge, and ϵ is the permittivity of the media surrounding the charge. The electric field has the units of newton per Coulomb or volt per distance.

The electric field around a point charge is illustrated in Fig. 1a, which shows the field strength or field density symbolized by density of the lines which is decreasing with the distance from the point charge. The electric field between two point charges of opposite charge is illustrated in Fig. 1b. In this case the two charges will attract each other. If they carry the same charge, they will repulse each other.

The electric field can be expressed by an electrical potential gradient. If the electrical potential varies over a certain distance, the electric field associated with this potential is given by the

Basic Electrochemical Relations in Membrane Processes: Electron Conductivity, Ion Conductivity, Ohm's Law, and Coulomb's Law,

Fig. 1 Schematic drawing illustrating the electric field lines (a) around a point charge and (b) between a positive and a negative point charge



Basic Electrochemical Relations in Membrane Processes: Electron Conductivity, Ion Conductivity, Ohm's Law, and Coulomb's Law, Fig. 2 Schematic drawing illustrating (a) the distribution of counterions

around a center-ion and (b) the potential and the concentration of excess charges around a center-ion as function of distance

derivative in the direction of the electric field (Kortüm 1957):

$$\operatorname{div} E = -\operatorname{div} \operatorname{grad} \varphi = \frac{4\pi}{\epsilon} \rho \quad (12)$$

Equation 12 is a special form of the Poisson differential equation which expresses the change of the electric field and the potential, respectively, around a single charge.

The effect of the electric field around a center-ion on the distribution of other ions in its surrounding and the decay of the electrical potential is illustrated in Fig. 2a, b which shows that the concentration of the excess charges around an ion

is decreasing exponentially with the distance from the center-ion.

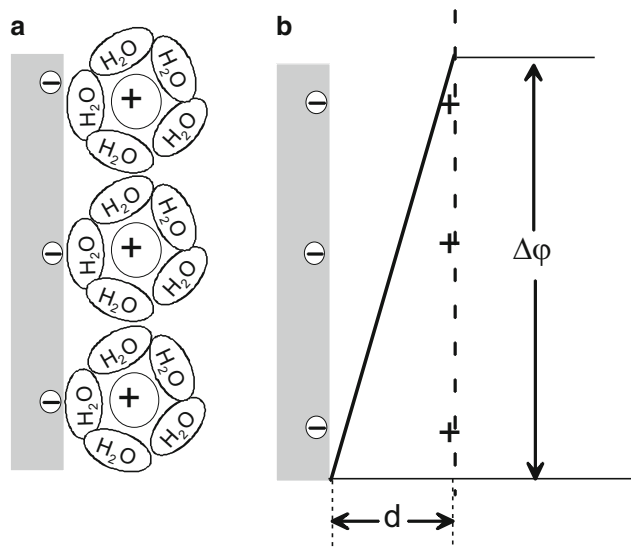
The electrical potential surrounding a center-ion is also decreasing with the distance from the center-ion, and it will reach zero at a certain distance. This distance is called the Debye length and marks the outer boundary of the ion atmosphere.

The Electric Double Layer at the Surface Membranes

When membranes with fixed charges at the surface are immersed into an electrolyte solution

Basic Electrochemical Relations in Membrane Processes: Electron Conductivity, Ion Conductivity, Ohm's Law, and Coulomb's Law,

Fig. 3 Schematic drawing illustrating (a) the closest approach of hydrated cations to the negatively fixed ions of the surface of a cation-exchange membrane and (b) the potential dissipation in the double layer according to the Helmholtz model



charge, they will generate an electric field directed into an adjacent solution and attract, due to the Coulomb forces, ions with the opposite charge. This leads to a layer on the membrane surface in which the concentration of the oppositely charged ions is higher than in the bulk solution. In many aspects the fixed charges of the membrane behave very similar to the charges surrounding a single charge in an electrolyte solution. These ions will form a layer at a certain distance from the membrane surface, which neutralize the fixed charges at the membrane surface. This double layer at the interface between the ion-exchange membrane and the adjacent solution is kept in place by the attraction force of the electrical potential generated by the fixed ions of the membrane and the dispersing force of the thermal motion. This double layer at the interface between the membrane and the electrolyte solution, which is important for certain electrokinetic phenomena such as electro-osmosis or streaming potential, can be described by several models (Wagenen and Andrade 1980). The simplest one of these models is the Helmholtz model.

The Helmholtz Double Layer Model

Helmholtz postulates that all counterions necessary to neutralize the surface charge of an ion-exchange membrane are aligned in a single

layer in parallel at a certain distance from the membrane surface. This distance is determined by the radius of the hydrated counterion as indicated in Fig. 3.

The Helmholtz model resembles a parallel plate capacitor where the charge is determined by the number of charges at the surface and in a plane parallel to the membrane surface. The relation between the surface charges, the potential between the negatively and positively charged layers, and their distance are given by the same equation, which describes the capacitance of a parallel plate capacitor (Starzak 1984), i.e.,

$$C = \epsilon \frac{A}{4 \pi d} = \frac{q}{U} \quad (13)$$

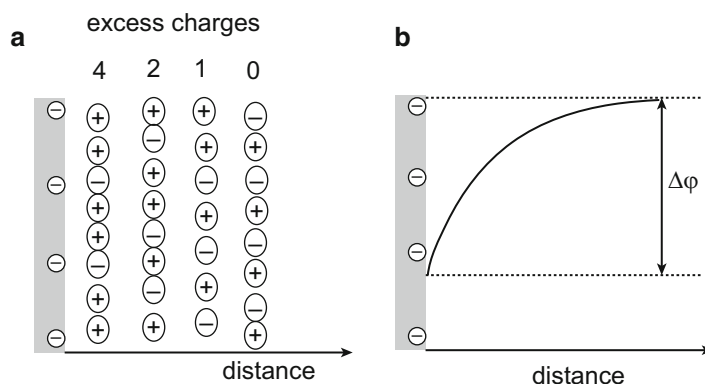
Here C is the capacitance, A is the area of the charge surface, d is the thickness of the Helmholtz layer, and q is the charge.

Introducing the surface charge density σ which is given by

$$\sigma = \frac{q}{A} \quad (14)$$

and replacing the voltage U by the potential difference $\Delta\phi$ between the two layers

$$U = \Delta\phi \quad (15)$$



Basic Electrochemical Relations in Membrane Processes: Electron Conductivity, Ion Conductivity, Ohm's Law, and Coulomb's Law, Fig. 4 Schematic drawing illustrating (a) the excess counterions in the

double layer as function of the distance from the membrane surface and (b) the potential dissipation as function of the distance from the surface of the membrane

give a relation between the thickness of the double layer d , the surface charge, and the potential difference in the double layer:

$$\Delta \varphi = \frac{4\pi d}{\varepsilon} \sigma \quad (16)$$

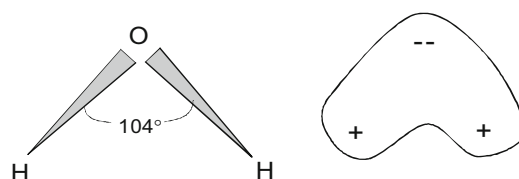
Here ε is the permittivity and σ is the surface charge density.

The Gouy-Chapman Double Layer Model

The Helmholtz model contains a number of rather drastic simplifications. For example, it assumes that the fixed ions form a homogeneous sheet and that the counterions form a complementary parallel sheet not affected by the thermal motion of the solution. In reality this is not the case.

In the Gouy-Chapman model, the counterions in the solution are no longer assumed to be aligned in a sheet but will occupy a finite volume in a mixture of cat- and anions. The total number of counterions in this volume is identical to the fixed charges of the membrane surface. Their distribution, however, is such that the area close to the membrane surface contains the largest excess of counterions as indicated in Fig. 4 and is very similar to the ion atmosphere around a single charge.

In analogy to the potential decay around a single charge, the potential at a certain distance from the membrane surface carrying fixed charges



Basic Electrochemical Relations in Membrane Processes: Electron Conductivity, Ion Conductivity, Ohm's Law, and Coulomb's Law, Fig. 5 Schematic drawing illustrating the structure of a water molecule indicating the dipole character due to the uneven distribution of the electrical charges within the molecule

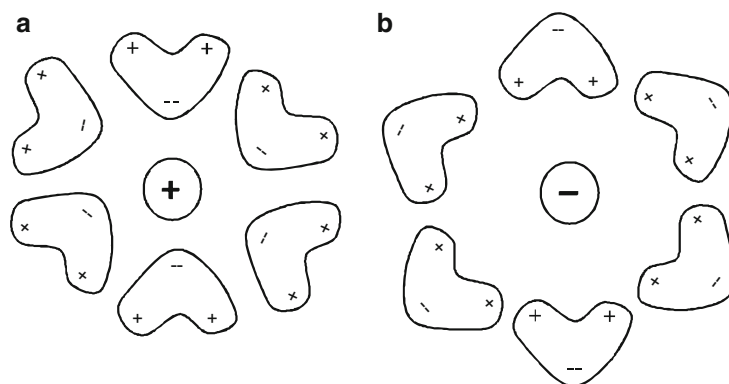
can be calculated by applying the Poisson equation which provides a relationship between the potential and the excess charges at a given point in the solution and under the assumption that the system obeys the Boltzmann statistic by

$$\Delta \varphi = \frac{\sigma x_D}{\varepsilon} \quad (17)$$

Here x_D is the Debye length which determines the thickness of the double layer. The Debye length is inversely proportional to the ion concentration of the solution. With increasing ion concentration, the Debye length is decreasing.

The boundary layer at the surface of membranes carrying fixed charges has a significant effect on the streaming potential and on the

Basic Electrochemical Relations in Membrane Processes: Electron Conductivity, Ion Conductivity, Ohm's Law, and Coulomb's Law, Fig. 6 Schematic drawing illustrating the distribution of water molecules (a) around a cation and (b) around an anion



B

electric osmotic water transport as well as on the so-called zeta potential (Lyklema 1995).

Electrical Dipoles and Intermolecular Forces

An electrical dipole consists of two opposite charges attached to a molecule and separated by a certain distance. An attraction of the charges is prevented by the rigidity of the molecular structure. The potential produced by the dipole is different from that produced by a single charge. The potential of a dipole with a single charge is decreasing with the distance by the square of the distance. The dipole momentum of molecules is measured in Debye [D] with $D = 3.33 \times 10^{-30} \text{ A s m}$. The dipole momentum varies substantially depending on the polarity of the molecules. It is 0 for a completely nonpolar molecule such as CCl_4 or H_2 and ca. 1.80 D for a polar molecule such as water (Atkins 1990). The high dipole momentum of the water is the result of the water molecule structure in which the hydrogen atoms are attached to one side of the oxygen atom as illustrated in Fig. 5.

The strong dipole momentum of water is also the reason for its good solubility properties for salts. The water dipoles tend to break the generally strong Coulomb forces between the negatively and positively charged ions of a salt crystal by surrounding the ions. Thus, in an aqueous solution, each ion is surrounded by a shell of water

molecules as indicated in Fig. 6(a) showing water molecules surrounding a cation and (b) water molecules surrounding an anion.

Another important result of the molecular interaction of water dipoles is the formation of the hydronium ions from protons and water. In water the proton recombines readily with the water molecule to the hydronium ion in which the three H atoms are no longer distinguishable and carry the positive charge together. The hydronium ion resembles a tripod with the three H atoms on one side and all equally apart from the oxygen atom. The rapid formation of the hydronium ion is the reason for the much faster transport of protons compared to other ions in an aqueous solution.

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Batch Diafiltration

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Batch diafiltration refers to a pressure-driven membrane filtration process in which a diluant (pure solvent) is added into the feed tank in order to enhance the degree of separation of macrosolutes from microsolutes. In batch diafiltration, in contrast to continuous diafiltration, the retentate stream is recirculated to the feed tank, and only the permeate stream is collected separately. During the operation, solute-free diluant is introduced into the feed tank to replace solvent losses as schematically illustrated in Fig. 1. The requirement for an effective separation is the utilization of a membrane which highly retains the macrosolute but permeable for the microsolite. Thus, depending on the application, microfiltration, ultrafiltration, nanofiltration, or even reverse osmosis membranes can be applied.

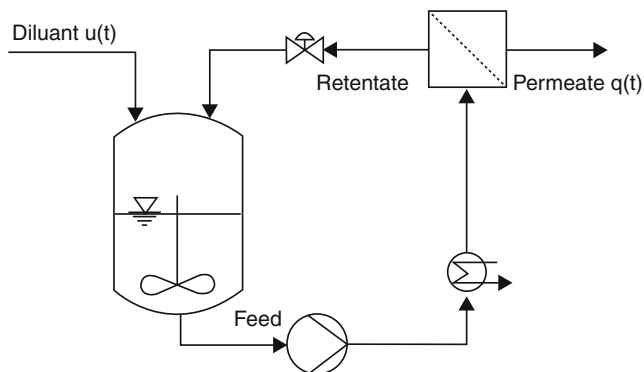
In its strict, original sense, the term batch diafiltration refers to a process that aims at removing the microsolutes from the process liquor. The standard way of achieving this purification goal is to employ a constant-volume diafiltration (CVD) process that is probably the most common type of batch diafiltration. In CVD, the feed volume is kept constant by continuously adding a diluant at a rate equal to the permeation rate.

It should be pointed out that the removal of microsolutes and the concentration of macrosolutes (i.e., the reduction of the volume of process liquor) are both required for most applications. The term batch diafiltration, in its broader sense, may stand for a batch filtration process that is designed to achieve the twin objectives of concentrating and purifying a multi-solute system according to a specific diluant utilization strategy. In this context, batch diafiltration is a complex process that may involve a sequence of consecutive operational steps.

A straightforward way of achieving the dual objectives of concentration and fractionation is to combine CVD with concentration mode operational steps (i.e., in which no diluant is added into the feed tank). A so constructed typical three-step process, also referred to as traditional diafiltration (TD), involves the following phases: (i) concentration mode to achieve an intermediate macrosolute concentration, (ii) constant-volume diafiltration to “wash out” the microsolite by a pure solvent introduced into the system, and (iii) further concentration to the final desired macrosolute concentration. Beside TD, a number of alternative strategies have been proposed. These include the sequential dilution diafiltration (SDD), intermittent feed diafiltration (IFD), variable-volume diafiltration (VVD), pre-concentration combined with variable-volume diafiltration (CVVD), and dynamic-volume diafiltration (DVD).

Diafiltration techniques differ in controlling the addition of the diluant in terms of quantity and duration. The differences between the various

Batch Diafiltration,
Fig. 1 Schematic representation of batch diafiltration configuration



Batch Diafiltration, Table 1 Diluant utilization strategies in batch diafiltration

Name	α - strategy
Constant-volume dilution	$\alpha = 1$
Traditional diafiltration	$\alpha = \{0, 1, 0\}$
Variable-volume diafiltration	$\alpha = \text{const}, 0 < \alpha < 1$
Preconcentration with variable-volume diafiltration	$\alpha = \{0, \alpha_1\}, \alpha_1 = \text{const}, 0 < \alpha_1 < 1$
Intermittent feed diafiltration	$\alpha = \{(0, \alpha_{\max})_n, 0\}$
Sequential dilution diafiltration	$\alpha = \{(\alpha_{\max}, 0)_n\}$
Dynamic-volume diafiltration	$\alpha = \alpha(t) \quad 0 \leq \alpha(t) \leq \alpha_{\max}$

n number of repetition

operations are best described by the proportionality factor α (i.e., the ratio of diluant flow $d(t)$ to permeate flow $q(t)$) as a function of operation time (Foley 2006). For instance, TD process is characterized with a sequence $\alpha(t) = \{0, 1, 0\}$ with two unknown switching times at the end of the first and of the second time interval. Similarly, CVVD process has two phases with constant α levels $\alpha(t) = \{0, \alpha_1\}$ and an unknown switching time. Table 1 shows the diluant control strategies applied in batch processing. Note that the best time-varying profile of diluant addition needs not necessarily be one of the arbitrarily predefined profiles. The diafiltration process, that is, designed by the evaluation of the optimal time-varying profile of the diluant flow, is referred to as dynamic-volume diafiltration (Paulen et al. 2012).

The governing differential equations for a generalized batch diafiltration process are given as

$$\frac{dc_i}{dt} = \frac{c_i q}{V} (R_i - \alpha), \quad c_i(0) = c_{i0}, \quad i = 1, 2$$

$$\frac{dV}{dt} = (\alpha - 1)q, \quad V(0) = V_0.$$

where c_i is the solute concentration in the feed tank, R_i the rejection of component i , and

V represents the feed tank volume. This initial value problem describes the evolution in time of the feed volume and the feed concentration of any solute under the assumption that the diluant is solute-free and the feed tank is well-mixed. Note that the time-dependent variables (i.e., permeate flux and the solute rejections) are, in a general case, a function of feed concentrations and may vary with operation conditions (temperature, pressure, cross-flow velocity, etc.).

The unique feature of realizing both concentration and fractionation puts membrane filtration in an attractive position and compares favorably with other separation methods or even with a sequence of consecutive unit operations. In comparison with continuous processes, batch operations are especially suited to small-scale operations, require less expensive automatic controls, and enable a reduced membrane area in order to reach the target (Baker 2004). Most batch plants operate under constant mechanistic membrane pressure adjusted simply by the retentate valve. There exist, however, other types of process control strategies in engineering practice, such as constant flux or constant wall concentration control (van Reis et al. 1997). These are normally employed when unfavorable side effects (e.g., enhanced fouling or product quality deterioration) occur that can be associated with the high concentration at the membrane wall.

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Bed-to-Wall Mass Transfer Limitations

Alessio Caravella

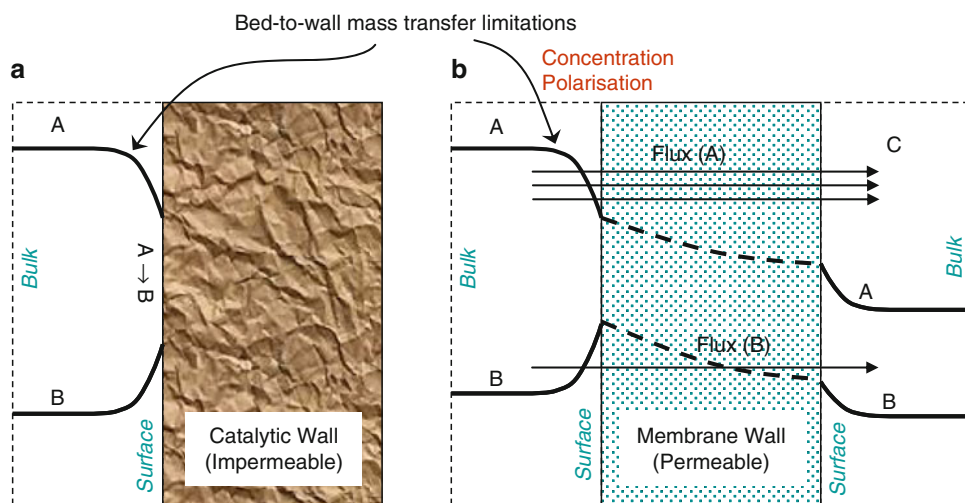
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Bed-to-wall mass transfer limitations. These phenomena, also referred to as “concentration polarization” in the field of *membrane technology* (Gallucci et al. 2011), are more generally related to the mass transfer resistance that a species encounters to reach an “active wall.” An “active wall” is a surface where physical and/or chemical transformations (including adsorption/desorption phenomenon and solubilization/desolubilization processes) occur.

The main cases of interest in chemical engineering are reported in Fig. 1. As for the former (Fig. 1a), an impermeable catalytic wall is considered, where the reactant species A reaches the catalytic surface and is transformed, as an

instance, into the product B, this being representative of all possible reactions. If the reaction rate is sufficiently fast, the transport through the gas phase becomes limiting and, thus, a significant concentration/pressure drop is generated, decreasing in fact the effective concentration of species A that can be involved in the surface reaction with respect to the bulk concentration.

As for the second case (*concentration polarization*, Fig. 1b), a membrane permeable to both species A and B is considered, with the species A being the one to separate and more permeable (higher transmembrane flux) than the species B. Because of the effect of the higher flux of the species A, the species B is “pushed” toward the membrane wall, generating in this way an obstacle for the species A to reach the surface. *Concentration polarization* is not desired for two main reasons. First, it causes a decrease in the permeation driving force of the species A, as the surface-surface concentration difference is smaller than the bulk-bulk one. Second, it tends to favor the permeation of the less-permeating species (B), causing the actual membrane *separation factor* to decrease.



Bed-to-Wall Mass Transfer Limitations, Fig. 1 Schematic representations of the two most common cases of bed-to-wall mass transfer limitations. (a) Case of impermeable catalytic wall on which a chemical

reaction takes place and (b) Case of membrane (permeable wall) through which all the components can, in general, pass. Membrane is supposed to be impermeable to the species C

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Beer Clarification

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In the traditional brewing process, the beer is clarified after fermentation and before maturation to remove mainly the remaining yeast but also microorganisms and haze. The conventional process for beer clarification is the combination of a high-speed separator followed by diatomaceous earth (DE)/kieselguhr filtration which is complemented in some cases by second filtration with PVP (polyvinylpyrrolidone) to obtain a very clear beer. The major challenge of the conventional process is related to the DE filtration because the DE can vary in quality and is problematic for handling and disposal since it is hazardous plus DE filtration generates large amounts of effluent. Alternatively, from its introduction in 2001 (Buttrick 2007) cross-flow microfiltration has established itself in the brewing industry with over 50 breweries worldwide adopting this DE-free beer filtration. Generally, three concepts are currently used in the industry:

1. Beer Membrane Filtration (BMF) by Pentair (previously Norit) – a system based on hollow fiber microfiltration cartridges without a high-speed separator as pretreatment
2. PROFi Membrane System by Pall and GEA Westfalia – a combination of hollow fiber microfiltration system with a high-speed separator as pretreatment

Beer Clarification, Table 1 Comparison of key parameters of beer filtered with DE filtration and microfiltration (Lipnizki 2005)

	Beer before filtration	Beer after DE filtration	Beer after microfiltration
Original extract [%]	11.40	11.37	11.39
Alcohol [%]	3.84	3.83	3.84
Color [EBC]	7.20	6.70	7.00
Viscosity [MPas]	1.62	1.57	1.56
Turbidity at 0 °C [EBC]	32.00	0.53	0.41

3. AlfaBright system by Alfa Laval and Sartorius – a process based on the combination of cassette microfiltration system with a high-speed separator as pretreatment

The membranes established for beer filtration are all polymeric microfiltration membranes based on polyethersulfone with 0.5–0.65 μm pores and beer capacities of 0.5–1.0 $\text{hl}/(\text{m}^2 \text{ h})$ (Buttrick 2007). The resulting beer quality from the membranes is similar or improved compared to the DE filtration; in Table 1 a comparison between beer filtered by DE and microfiltration membranes is given. Other membranes, e.g., ceramic membranes, have been tested for beer filtration but so far have not established themselves on the market. The key difference between the three concepts is the use of a high-speed separator as pretreatment. In the BMF system a retentate tank is used to collect the beer solids, while both the PROFi and the AlfaBright systems are using high-speed separators as pretreatment before the membrane to remove the beer solids and thus eliminating the need for a retentate tank. The systems can be typically run in batch or continuous operation depending on the size and requirements of the individual brewery. In batch operation, the complete system shifts from filtration into cleaning mode after each batch. Plants with continuous operation are arranged in

skids/blocks and use sequential cleaning which allows for some skids/blocks to be in standby cleaning mode, while other blocks are in filtration mode. The major challenges for cross-flow membrane beer filtration are the relatively high investment costs and complexity of the process when compared to DE filtration and the increasing availability of alternative DE-free filter aids.

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Beer Dealcoholization

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In the last decades the demand for low alcohol and alcohol-free drinks increased, e.g., in Germany the annual consumption of alcohol-free drinks nearly doubled from 130.4 l per person in 1980 to 248.2 l person in 1999, while the annual consumption of alcoholic drinks declined from 179.5 to 156.3 l during the same period (Gebhardt 2001). Conventionally beer can be dealcoholized by distillation, but additionally the membrane process reverse osmosis and dialysis have established themselves for the partial dealcoholization of beer by eight to ten times. The key advantage of membrane processes over distillation is that beer can be dealcoholized at low temperatures typically 78 °C to minimize the effect of temperature on the beer flavor resulting in high-quality low alcohol beer, which can be bottled after final sterile filtration.

Reverse osmosis is typically carried out in spiral wound modules, and the dealcoholization

process based on reverse osmosis can be divided into four individual operations which are typically carried out in batch mode:

1. **Pre-concentration:** In this step the volume of the feed beer is reduced. The beer is passed through the membrane modules and is then recycled to the batch tank. The permeate – water and alcohol – is removed from the process, while retentate, concentrated beer and flavors, is returned to the batch tank.
2. **Diafiltration:** This step is similar to the pre-concentration step but diafiltration water – desalted and deoxygenized water – is added to wash out the alcohol. The amount of diafiltration water added balances the amount of permeate removed from the process, and thus, the level in the batch tank remains constant. This operation is continued until the desired alcohol concentrations in the beer are achieved.
3. **Alcohol adjustment:** In this step, the taste and alcohol content is fine-tuned by addition of desalted and deoxygenized water.
4. **Posttreatment:** In order to give the beer its specific character and to balance taste losses due to removal of the taste carrier alcohol, the CO₂ levels can be adjusted, and hop extract, syrup, or other flavor enhancers are added.

As an alternative to reverse osmosis, dialysis can be used for the dealcoholization of beer. Commonly, hollow fiber modules are used for dialysis allowing the beer to flow on one side of the membrane and water as dialysate on the other side. The process is normally operated in counter-current flow to maximize the concentration gradient over the dialysis membrane and thus the driving force of the dialysis process. The dialysate is constantly recycled over a steam stripping column to remove the alcohols, thus maintaining the driving force of the process while minimizing the dialysate consumption. In addition, in order to minimize CO₂ losses, the feed pressure should be selected close to the CO₂ saturation pressure, and small amounts of the CO₂ should be added to the dialysate (Branyik et al. 2012).

Furthermore, osmotic distillation for beer dealcoholization (Russo et al. 2013) and pervaporation for aroma recovery can be considered as part of the beer dealcoholization process (del Olmo et al. 2012), but so far these processes are not commercialized.

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Beer Maturation

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In the beer production process, the clarified and cooled wort from the brewhouse is transferred together with yeast to the fermentation tanks for the primary fermentation which converts the fermentable sugar into alcohol and CO₂. The resulting “green beer” undergoes a second fermentation – beer maturation – under addition of sugar or fresh yeasted wort. During the maturation, the residual fermentable sugars in the “green beer” will be converted to alcohol and the beer will be saturated with CO₂. After the fermentation, the beer is clarified and stored in the bright beer cellar. Remaining in the fermentation tanks are tank bottoms – a mixture of settled yeast cells and beer – which are equal approx. 1.5–2.0 % of

the fermentation tank volume. In the past this beer in the tank bottom would be considered lost since it could not be added to the main beer stream. However, using microfiltration with tubular ceramic membranes or plate-and-frame modules with polymeric membranes, it is possible to recover a high-quality beer which can be blended with the main beer stream going toward clarification and storage. Using microfiltration membranes with pores of 0.4–0.5 µm, it is possible to retain the yeast and allow the beer to pass the membrane without any major impact on the quality of the beer. In this process, the yeast in the tank bottoms is concentrated from 7 % to 10 % DM to approx. 20 % DM and thus 50–70 % of the beer in the tank bottoms can be recovered. The yield of recovered extract and alcohols can be further maximized if diafiltration water is added. Recovering beer from tank bottoms can increase the output of an average brewery by 1 % of its annual production or 24,000 hl extra for a brewery with an annual output of 2 million hl (Lipnizki 2005). The amortization for a microfiltration beer recovery unit is typically 1–2 years.

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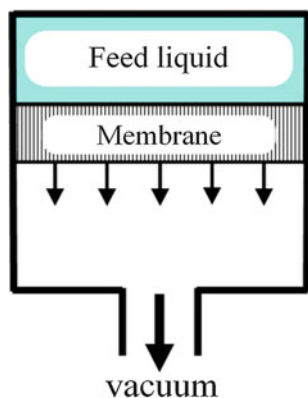
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Benzene and Cyclohexane Separation

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Benzene/Cyclohexane Separation

In the petrochemical industry, the separation of benzene (Bz) and cyclohexane (Chx) is the most



Benzene and Cyclohexane Separation, Fig. 1 Principle of pervaporation (PV)

important and difficult processes. Chx is produced in benzene hydrogenation units under Ni or Pd catalyst. The unreacted Bz is remained in the reaction mixture and must be removed to produce pure Chx. The separation of benzene and Chx is very difficult by a conventional distillation because close-boiling point mixtures are formed in the entire range of their compositions. At present, azeotropic distillation and extractive distillation are applied to this separation. These distillations, however, are complex and need high energy consumption. In the industry of Chx production, the conventional Bz/Chx separation processes are strongly required. Therefore, many studies have investigated the PV properties of polymer membranes for Bz/Chx separation.

Pervaporation (PV) is a promising membrane technique for the separation of organic/organic mixtures, as PV can be used to separate organic liquid mixtures such as azeotropic and close-boiling point mixtures. The separation mechanism in PV is not based on only relative volatility of components in distillation but on the difference in sorption and diffusion properties of the feed substances.

Figure 1 illustrates the principles of PV. In this separation process, when a liquid mixture is fed to the upstream side of a polymer membrane and the downstream side is evacuated, a component in the

feed mixture can preferentially permeate through the membrane. In a PV process, differences between the solubility and diffusivity of the mixture components in the polymer membrane and the relative volatility of the permeants determine the permeability and selectivity (Binding et al. 1961; Aptel et al. 1974). In general, PV exhibits the following characteristics (Uragami 2006, 2010):

1. Selective transport across the nonporous membrane is achieved by a three-step process of solution, diffusion, and evaporation.
2. Because the driving force for permeation is the vapor pressure for each component rather than total system pressure, this method is effective for separation of organic liquid mixtures with high osmotic pressure.
3. PV can be applied to the separation and concentration of mixtures that are difficult to separate by distillation. For example, it is useful for the separations of azeotropic mixtures, close-boiling point mixtures, and structural isomers.
4. PV can be used for the removal of certain components in equilibrium reactions.
5. Polymer membrane compaction, a frequent problem in high-pressure gas separations, is not encountered in PV because the feed pressure is typically low.

A side-chain liquid-crystalline polymer (LCP) was synthesized by the addition of mesogenic monomer to poly(methylsiloxane) with a Pt catalyst. When Bz/Chx mixtures were permeated through the LCP membranes by PV at various temperatures, the permeation rate increased with increasing benzene concentration in the feed solution and permeation temperature. Although the LCP membranes exhibited Bz/Chx selectivity, the mechanism responsible for the permeation and separation of the Bz/Chx mixtures was different in the glassy, liquid-crystalline state versus the isotropic state of the LCP membranes. These results suggest that the Bz/Chx selectivity was

moderately influenced by the change in LCP membrane structure (i.e., a state transformation). The balance between the orientation of the mesogenic groups and the flexibility of the siloxane chain is very important with respect to permeability and Bz/Chx selectivity (Inui et al. 1997, 1998). When benzene/cyclohexane, toluene/cyclohexane, and *o*-xylene/cyclohexane mixtures were subjected to PV through an LCP membrane in the liquid-crystalline state, the permeation rate increased with increasing temperature and the LCP membrane exhibited selectivity for the aromatic hydrocarbons. The permeation rate and selectivity of the LCP membrane for each mixture decreased with increasing molecular size of the aromatic hydrocarbon in the binary feed mixture (Inui et al. 1998). When Bz/Chx mixtures were permeated through nematic and smectic side-chain liquid-crystalline polymer (*n*- and *s*-LCP) membranes under various conditions during PV, the *n*- and *s*-LCP membranes exhibited Bz/Chx selectivity. The selectivity of the *n*-LCP membrane changed from solubility-selectivity controlled to diffusion-selectivity controlled upon the state transformation of the membrane, induced by an increase in the permeation temperature. In contrast, the selectivity of the *s*-LCP membrane was governed by diffusion selectivity regardless of the state of this membrane. At low permeation temperatures, the *n*-LCP membrane in the liquid-crystalline state exhibited lower permeability but higher selectivity than the *s*-LCP membrane. However, at high permeation temperatures, the relationship between the permeability and Bz/Chx selectivity of the *n*-LCP and *s*-LCP membranes in the liquid-crystalline state was reversed. These results are a result of differences in the chemical and physical structure of the *n*-LCP and *s*-LCP membranes (Inui et al. 1998).

The PV properties of a series of cross-linked 4,4'-hexafluoro-isopropylidene dianhydride (6FDA)-based copolyimide membranes for the separation of Bz/Chx mixtures were investigated (Ren et al. 2001). The glassy, highly rigid copolyimides were obtained by polycondensation

of 6FDA with various diamines. To obtain high permeability as well as high selectivity, a combination of the diamines 2,3,5,6-tetramethyl-1,4-phenylene diamine (4MPD), 4,4'-hexafluoroisopropylidene dianiline (6FpDA), and 3,5-diaminobenzoic acid (DABA) as monomers with a crosslinkable group was used. Cross-linking is necessary to prevent undesirable swelling effects, which generally occur with non-cross-linked polyimides, especially if high benzene concentrations are reached during PV. The degree of cross-linking was kept constant at 20 %, whereas the ratio of the diamine monomers 6FpDA and 4MPD was varied. The PV experiments were performed at 60 °C, using Bz/Chx mixtures with benzene concentrations covering the entire concentration range. All of the cross-linked polymers had excellent chemical and thermal stability in the PV experiments. In all cases, conditioning of the membrane samples with pure benzene was a suitable pretreatment to enhance the permeation rate without decreasing the Bz/Chx selectivity significantly. For the most promising membrane material, 6FDA-4MPD/DABA of 4:1 cross-linked with ethylene glycol, the PV experiments were performed with a benzene/cyclohexane feed mixture of 50/50 (w/w) over a temperature range between 60 °C and 110 °C to determine the effect of temperature on the separation characteristics.

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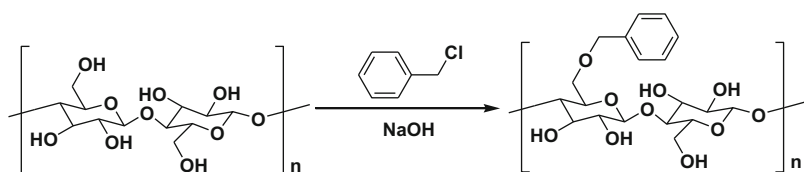
Benzyl-Modified Cellulose

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Benzyl-modified cellulose contains covalently bonded benzyl groups in the cellulose structure, typically produced by etherification of hydroxyl groups (Bowry and Rintelen 1998) shown in Fig. 1.

Benzyl-Modified Cellulose,

Fig. 1 Synthetically modified cellulose from benzyl-modified cellulose by etherification



The benzylation of cellulose can lead to several useful applications. For example, in blood hemodialysis, membrane filtration is a key process for the replacement of renal function in uremic patients. The hydroxyl groups in cellulose can activate complement function, which is an undesirable process in hemodialysis. A certain amount of the substitution of hydroxyl groups with benzyl groups, being known as synthetically modified cellulose (SMC), can help minimize the complement activation, by balancing the hydrophilic and hydrophobic domains in the cellulose structure (Hoenich et al. 1997).

Another application of benzylation of cellulose is the fabrication of natural fiber composites by the surface modification of cellulose through the route shown in Fig. 1 (Lu et al. 2004). The fiber composites exhibit excellent thermal formability and mechanical properties, enabled by the benzyl cellulose skin layer and natural cellulose core (Zhang et al. 2005).

It should be noted that the benzylation of cellulose, as mentioned above, can produce a heterogeneous structure with only the skin of the cellulose structure being modified. A homogeneous benzylation of cellulose has been achieved when ionic liquids were used as the solvent for cellulose (Gericke et al. 2012). *N*-alkylpyridinium chlorides can be used to dissolve cellulose and then react with benzyl groups, resulting in benzyl cellulose with a high degree of substitution. It is possible that the surface modification of fibrous mats with benzyl cellulose can be achieved by surface coating and thereby forming a non-covalently bonded modification approach (Ma et al. 2014).

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Bichromal Particles Synonym: Two-Colored Particles

► Encapsulation Application

Bilberry Aroma Recovery by Pervaporation

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Introduction

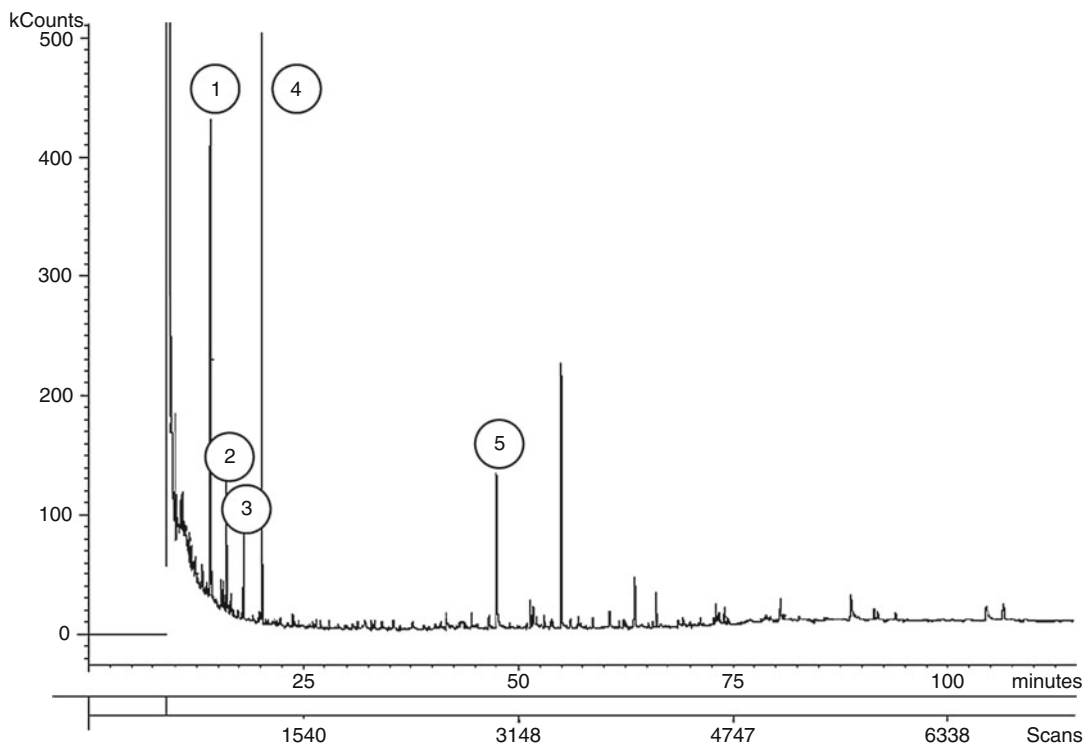
Pervaporation (PV) is a membrane-based technology largely studied for aroma compound recovery and concentration in the food industry (Pereira et al. 2006). At least two PV pilot plants for aroma compound recovery have been built at Membrane Technology and Research (MTR)

Inc., California (EEUU), and Agrotechnology & Food Innovations (A&F) in the Netherlands (Willemsen et al. 2004), and theoretical studies assessing the recovery and concentration of aroma compounds by means of PV have demonstrated the viability of this technology at industrial scale (Karlsson et al. 1998; Lipnizki et al. 2002a, b; Trifunovic et al. 2006). During the PV, the aroma compounds contained in a liquid or feed phase permeate selectively through a dense hydrophobic membrane due to the chemical potential gradient caused by a reduction of the component partial pressure in the permeate side. The aroma compounds are preferentially transported through the membrane according to their affinity to the membrane material and their mobility in the membrane matrix, which is the hypothesis of the most accepted mass transport mechanism in PV known as solution-diffusion.

Bilberry (*Vaccinium myrtillus* L.) is a species of shrub and is native from Europe, northwest regions of North America, and Northern Asia (Morton and Macleod 1990). The international markets' demand of bilberry's extract has been steadily growing in the recent years (Foster and Blumenthal 2012). The major aroma compounds present in crushed bilberry were identified by gas chromatography-mass spectroscopy (GC-MS). The results are shown in Fig. 1. Trans-Hex-2-en-1-ol was characterized as one of the impact flavor of the bilberry (von Sydow and Anjou 1969).

Membrane Material and Module Configurations

The most typical organophilic membrane materials employed in PV of aroma compounds in the literature are polydimethylsiloxane (PDMS) and polyoctylmethylsiloxane (POMS). POMS membranes present higher enrichment factors for aroma compounds than PDMS albeit not significantly different. Nonetheless, PDMS membranes are largely more studied due to their stability during operation and good properties of processing (Karlsson and Trägårdh 1993; Lipnizki et al. 1999; Uriaga et al. 1999).



Bilberry Aroma Recovery by Pervaporation, Fig. 1 GC-MS chromatogram of the crushed bilberry: (1) trans-hexenal, (2) 2-butyl-1-octanol, (3) 1-hexanol,

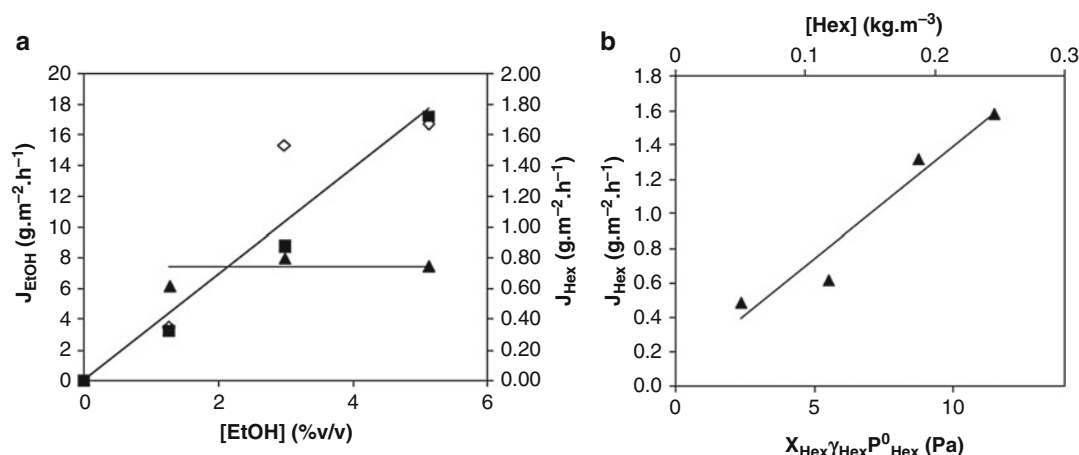
(4) trans-Hex-2-en-1-ol, and (5) 1-hexadecanol (Adapted from (Garcia et al. 2008))

With regard to the membrane module configurations, plate-and-frame is the most employed in literature for laboratory scale studies for their simplicity and versatility for the evaluation of different membrane materials. However, the hollow fibers membrane (HFM) module configuration presents important advantages, such as higher contact area per unit volume of membrane module and thus higher compactness of the equipment and easier operation at industrial scale (Urtiaga et al. 1999, 2002; Tasselli et al. 2007).

Influence of Process Variables

Using a model ternary solution (water/ethanol/trans-Hex-2-en-1-ol), the process variables that exerted an important influence on the PV performance of the impact aroma compound (trans-Hex-2-en-1-ol) when using a PDMS HFM module with the characteristics presented at (Garcia et al. 2008) were:

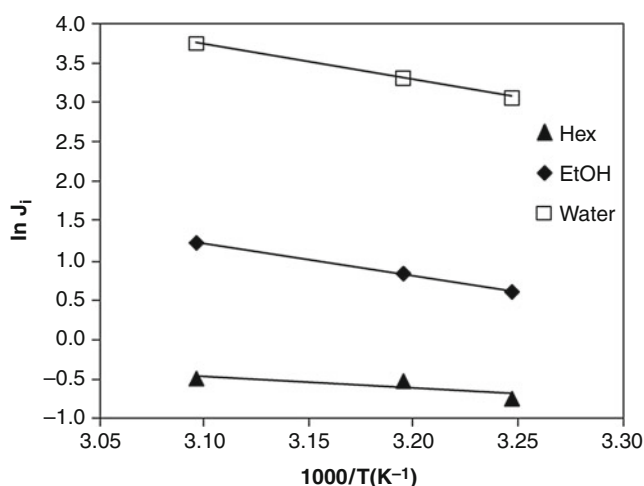
- (i) The feed composition (ethanol and aroma compound). The results are presented in Fig. 2. As expected, ethanol flux, J_{EtOH} , increased linearly with higher ethanol content in the feed, while in contrast, aroma compound partial flux, J_{Hex} , remained independent on ethanol concentration but presented a linear dependency with its own concentration in the feed solution. The major component flux, water, was independent on both ethanol and aroma compound composition. The enrichment factors found for the aroma compound, β_{Hex} , varied from 98 to 201.
- (ii) The feed temperature, studied in the range $35\text{ }^{\circ}\text{C} < T < 50\text{ }^{\circ}\text{C}$. The components' partial fluxes (water, ethanol, and trans-Hex-2-en-1-ol) were found to follow an Arrhenius dependency with temperature as plotted in Fig. 3.



Bilberry Aroma Recovery by Pervaporation, Fig. 2 (a) Effect of ethanol concentration in the feed on the permeation flux of the ethanol in (■) binary water/ethanol and (◇) ternary water/ethanol/Hex mixtures, and (▲) flux of trans-hex-2-en-1-ol in ternary mixtures

[Hex] = 0.1 kg.m⁻³, $T = 50^\circ\text{C}$ and $Re = 772$. (b) Effect of trans-hex-2-en-1-ol partial pressure in the feed on its permeation flux at 50°C , $Re = 772$, and [EtOH] = 1%v/v (Adapted from (Garcia et al. 2008))

Bilberry Aroma Recovery by Pervaporation, Fig. 3 Effect of the feed temperature on the partial fluxes of the components when $Re = 772$, [Hex] = 0.1 kg.m⁻³, and [EtOH] = 1%v/v (Adapted from (Garcia et al. 2008))



In the present application and working under laminar flow rate conditions, $203 < Re < 772$, the aroma compound transfer flux was independent on the feed flow rate. This indicated that the concentration polarization phenomena in the feed boundary layer was negligible in comparison with the aroma compound mass transfer resistance in the membrane which normally occurs with high membrane thickness, i.e., 127 and 160 μm (Peng and Liu 2003;

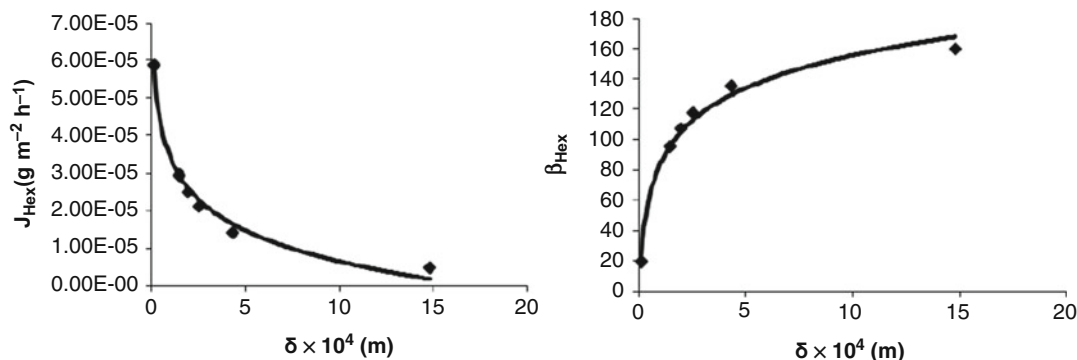
Kanani et al. 2003), similar to the membrane thickness herein studied, 196 μm .

PV of Multicomponent Systems

PV of multicomponent systems of the bilberry characteristic aroma flavor was performed theoretically by means of simulation considering the composition in Table 1 and commercial PDMS HFM modules. The membrane area considered was $A_m = 0.0056 \text{ m}^2$ and the membrane

Bilberry Aroma Recovery by Pervaporation, Table 1 Feed composition (found in Hirvi and Honkanen 1983), and simulation results of the permeate composition, enrichment factors, and partial fluxes in the bilberry multicomponent system after PV with a PDMS HFM module at 30 °C and a membrane area $A_m = 0.0056 \text{ m}^2$ (Diban et al. 2008)

Component	Feed composition, C_i^F (mg.kg ⁻¹)	Permeate composition, C_i^P (mg.kg ⁻¹)	β_i	J_i (g.m ⁻² .h ⁻¹)
Trans-Hex-2-en-1-ol	0.01	1.21	120.6	3.78×10^{-5}
n-Hexanol	0.02	4.74	236.9	14.9×10^{-5}
Trans-Hex-2-en-1-al	0.06	2.78	46.3	8.70×10^{-5}
Linalool	0.004	0.20	49.3	0.62×10^{-5}
Phenyl acetaldehyde	0.003	0.02	5.5	0.05×10^{-5}
Benzyl alcohol	0.08	0.33	4.2	1.05×10^{-5}
Cis-Hex-3-en-1-ol	0.06	1.64	27.4	5.15×10^{-5}
Ethanol	7800	106,934	13.7	2.51
Water	992,200	893,057	0.9	20.9



Bilberry Aroma Recovery by Pervaporation, Fig. 4 Change of the partial flux of trans-Hex-2-en-1-ol, J_{Hex} , and enrichment factor, β_{Hex} , with the membrane

thickness, δ . $T = 30 \text{ }^\circ\text{C}$, $[\text{Hex}] = 10^{-5} \text{ kg.m}^{-3}$, $[\text{EtOH}] = 1\% \text{ v/v}$, $Re \sim 6 \times 10^5$, $A_m = 0.0056 \text{ m}^2$ (Adapted from Diban et al. 2008)

thickness, δ , was $1.96 \times 10^{-4} \text{ m}$. Further details of the simulation conditions can be found in (Diban et al. 2008). The results of the simulation are collected in Table 1. There is a clear change in the component profile from the feed solution to the permeate aroma compound concentrate.

Moreover, the theoretical evaluation of the influence of the membrane thickness, δ , on the performance of the PV of trans-Hex-2-en-1-ol was performed. The results are plotted in Fig. 4. From these results, it is extracted that a commercially available membrane with a thickness of $1.48 \times 10^{-4} \text{ m}$ led to a compromise situation with important impact aroma compound enrichment factors $\beta_{Hex} \sim 90$ and adequate fluxes $J_{Hex} \sim 3 \times 10^{-5} \text{ g.m}^{-2}.\text{h}^{-1}$.

Future Directions

1. Experimental assessment of the behavior of real solutions to evaluate (i) the interaction between different molecules during PV and (ii) the aroma profiles in the permeate.
2. Integration of a sensory evaluation of the quality of the aroma compound concentrate that, independently of the aroma profile, is mainly affected by the presence of the impact aroma compounds in the permeate.
3. Evaluation of other membrane materials that reduce water mass transfer and enhance the aroma compound enrichment factors with the minimum flux reduction, such as POMS.

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Bimetallic Electrocatalyst for Fuel Cells

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General Requirements for Fuel Cells

Most of the known today fuel cell systems (e.g., automotive, portable applications, backup power, etc.) have common requirements that include reduction in costs, improvement in performance and durability, increase in tolerance toward impurities in the feed fuel, etc. (Vielstich et al. 2003a; Debe 2012).

Pt-based Electrocatalyst: Key Component

The platinum-based electrocatalyst used in PEM (proton-exchange membrane, also called polymer electrolyte membrane) fuel cells, PAFC (phosphoric acid fuel cell), and DMFC (direct methanol fuel cell) is one of the key components and directly influences performance, durability, costs, etc. More specifically, in the PEM fuel cell, the oxygen reduction reaction (ORR) occurring at the cathode is known to have slow kinetics, leading to large cathodic overpotential losses under typical operating conditions. In the case of specific application of PEM fuel cells, when hydrogen is produced from a reformat, an additional requirement such as tolerance of the anode electrocatalyst toward the traces of CO in the feed fuel stream must also be met. In order to reduce

costs of the fuel cells, an increased mass activity of the cathode electrocatalyst is required that would allow a decrease in the amount of the electrocatalyst in a fuel cell device.

Advanced Electrocatalysts

A search for better ORR electrocatalysts for PEM fuel cells that meet advance requirements has resulted in the development of various Pt-based bimetallic compounds (these can include alloys or intermetallic systems). It is believed that the improved performance (i.e., activity enhancement) of bimetallic alloys as electrocatalysts could be explained by the structural modification of Pt 5d orbital, coordination number of Pt, and modification in adsorption of oxygenated species from the electrolyte to the Pt or the alloying metal. For example, alloying results in a lattice contraction, leading to a more favorable Pt-Pt distance for the dissociative adsorption of oxygen (Vielstich et al. 2003b; Zhang 2008).

Pt+Cr, Pt+Ni, and Pt+Co bimetallic electrocatalysts have been demonstrated to show two- to threefold increase in their activities for ORR. The activation energy for oxygen reduction was also shown to be lower than that in Pt. However, it is also well recognized that these bimetallic electrocatalysts are subject to significant degradation rates (sintering/dissolution) as well as carbon-support corrosion under specific voltage cycling conditions that are common for automotive drive cycles during fuel cell startup and shutdown.

A lot of efforts have also been made during the last two decades to improve anode electrocatalyst in fuel cells that are designed to use hydrogen obtained by means of reforming other fuels. In that case an anode electrocatalyst is required for hydrogen oxidation reaction to take place in the presence of CO, as well as to improve performance of the methanol fuel cells. The focus has been on the development of bimetallic platinum-based electrocatalysts to reduce the amount of adsorbed CO and/or to improve performance of

electrooxidation of CO. Many metals have been considered for modifying the activity of the platinum catalyst, but only a few of them (Ru, Ir, Sn, Mo, etc.) lead to improved performances. The most studied bimetallic electrocatalyst is the family of Pt/Ru alloys, which enhance greatly the rate of oxidation of many alcohols (methanol, ethanol, etc.).

Current Trends

Research and development in the area of bimetallic and ternary electrocatalysts is ongoing. The trend is to make use of unique nanoscale structural effects that can be observed in structurally modified alloys (e.g., de-alloyed Pt-based catalysts) and intermetallic systems to enhance greatly ORR. These include novel structures observed in thin film extended surfaces (Stamenkovic et al. 2007; Debe 2012) as well as a multilayer Pt-skin surface (Wang et al. 2011, 2012).

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Bioactive Compounds

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“Bioactive compounds” are extranutritional constituents that typically occur in small quantities in foods and can be shown to have an effect on human health.

Bioactive compounds are also referred as *nutraceuticals*, a term that reflects their existence in the human diet and their biological activity.

They consist of a wide range of chemical compounds with different structures, physiological activities, and molecular mass between 200 and 1000 Da (Pennington 2002).

Typical bioactive compounds include:

- Carotenoids (α -carotene, β -carotene, lycopene, lutein)
- Flavonoids (flavanols/flavans, isoflavones/isoflavonoids, flavanones, flavones, anthocyanins)
- Phenolic acids (cinnamic acid, caffeic acid, chlorogenic acid, p-coumaric acid, ferulic acid, citric acid, ellagic acid, vanillic acid, hydroxytyrosol, tyrosol, oleuropein)
- Plant sterols (beta-sitosterol, campesterol, phytosterol, saponin, squalene, stigmasterol, stanol)
- Resveratrol
- Probiotics
- Omega-3 fatty acids (α -linoleic acid)
- Proteins
- Organosulfur compounds (allyl/diallyl sulfides)
- Indoles
- Monoterpenes (limonene, perillyl alcohol)

Bioactive compounds have been intensively studied in order to evaluate their effects on human health, and numerous methodological approaches have been implemented to clarify their biological effect and mechanism of action.

For example, phenolic compounds and flavonoids from vegetable sources such as cereals, legumes, olives, and fruits exhibit antioxidant, anti-inflammatory properties, and different studies have reported protective associations between flavonoids and cardiovascular disease (CVD) and cancer.

Hydroxytyrosol, one of the most important phenolic compounds in olives, olive oil, and olive mill wastewaters, presents a strong antioxidant and anticancer properties.

Resveratrol, found in red wine, has antioxidant, antithrombotic, and anti-inflammatory properties and inhibits carcinogenesis. Lycopene, a potent antioxidant carotenoid in tomatoes and fruits, presents a protection against prostate and other cancers and inhibits tumor cell growth in animals.

Organosulfur compounds in onions and monoterpenes in citrus fruits have shown anticarcinogenic actions in experimental models, as well as cardioprotective effects.

Bioactive compounds are the main source of new drugs, functional food, and food additives. In fact, more than 80 % of food active compounds and more than 30 % of drugs are produced from bioactive natural products and the annual growth rate of natural drugs is 20 %.

As a result, the research of appropriate techniques for the separation of these compounds from complex matrix has attracted much attention in the last years. Generally, the separation of target compounds includes extraction and purification steps.

Several techniques have been proposed for the separation of bioactive compounds including solvent extraction, irradiation-assisted extraction, ultrasound-assisted extraction, heat treatment, enzyme-assisted extraction, supercritical fluid extraction, resin-based extraction, and chromatography purification techniques (Azmir et al. 2013).

These separation methods are characterized by some drawbacks, such as the degradation of the compounds of interest due to high temperatures and long extraction times (as in solvent

Bioactive Compounds, Table 1 Typical membrane operations for the separation of bioactive compounds from different sources

Bioactive compounds	Examples	Sources	Membrane processes
<i>Flavonoids</i>	Quercetin, catechin	Apple juice, tea, red wine	MF, UF, NF, RO
	Narirutin, naringin, hesperidin, neohesperidin	Citrus juices	MF, UF, NF, RO
	Apigenin, luteolin	Artichoke wastewaters	UF, NF, RO
	Cyanidin, cyanin, myrtillin	Red orange and pomegranate juices	MF, UF, NF, RO
<i>Carotenoids</i>	α -Carotene, β -carotene	Palm oil, carrot juice	MF, NF
	Lycopene, lutein	Carrot, kiwifruit, and tomato juices	MF, UF
<i>Phenolic acids</i>	Caffeic acid, chlorogenic acid, p-coumaric acid, ferulic acid	Apple juice, olive mill, and artichoke wastewaters	MF, UF, NF, RO
	Citric acid	Citrus juices	MF, UF, NF, RO
	Ellagic acid	Blackberry juices	UF, NF
	Tyrosol, hydroxytyrosol oleuropein, gallic acid	Olive mill wastewaters	MF, UF, NF, RO
<i>Proteins</i>	α -Lactalbumin, β -lactalbumin, bovine serum albumin (BSA)	Whey, milk	MF, UF, NF
	Immunoglobulines	Egg yolk	UF
	Phycocyanin	Marine organisms (microalgae)	UF, NF, RO
<i>Omega-3 fatty acids</i>	Linoleic acid	Fish-processing wastes	MF, UF, NF

extractions) and health-related risks. In addition, they involve high capital costs.

Recently, membrane technology has attracted attention as an alternative molecular separation technology due to its advantages such as high efficiency, simple equipment, easy scale-up, and low energy consumption. In general, membrane separations can operate under mild conditions of temperature, pressure, and shear stress, therefore preserving the biological activity of the compounds to be recovered and the properties of the original product; they do not require any extraction mass agents such as solvents, avoiding product contaminations and the need for subsequent purification.

Particularly, pressure-driven membrane technologies such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are extremely efficient for the separation, fractionation, purification, and

concentration of different classes of bioactive compounds from a complex mixture and in the recovery of intermediate compounds (Cassano and Drioli 2014).

Membrane operations in sequential design are particularly suitable alternative for recovery/concentration of bioactive phenolic compounds from fruit juices and food-producing wastewaters. MF and UF are typically applied for preliminary treatment while the purification and concentration steps are usually performed by NF and RO membranes.

The separation of bioactive proteins from milk and marine sources with UF and NF membranes results in high selectivity due to the large molecular weight differences between the target compounds.

Typical examples of membrane operations used for the separation of bioactive compounds are summarized in Table 1.

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Bioadhesion to Membrane Surface

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Bioadhesion to membrane surface refers to the special interaction between biological organisms to membrane surfaces. The term “bioadhesion” generally describes the adherence of materials (natural or synthetic) to biological surfaces or the firm attachment of biological substances (such as microorganisms, proteins, cells, biomolecules, etc.) on material surfaces (Huang et al. 1999). As an interface phenomenon, bioadhesion is similar to conventional adhesion, except for the special characteristics of biological organisms and surfaces. As such, this term covers the adhesive properties of both synthetic components and the natural surfaces (such as cells) (Jacek et al. 1999). Bioadhesion also includes the use of bioadhesive (natural polymeric materials, such as proteins and carbohydrates) to stick two surfaces together (Palacio and Bhushan 2012). In medicine and biology, sometimes bioadhesion is also used as a synonym of mucoadhesion, which refers to the process whereby synthetic and natural macromolecules adhere to mucosal surfaces in the body

(Woodley 2001). Bioadhesion to membrane surface is often related with biofouling of membrane surface and thus receives much attention in membrane technology, particularly in biomedical membrane separation.

In blood-contact membrane separation, for the blood-incompatible membrane materials, the platelets in the blood tend to accumulate and adhere onto membrane surface due to a biological immune reaction. As a result, thrombus formation may form and further result in some serious complications. Therefore, the blood-contact membranes such as hemodialysis membranes often need be modified to prevent the adhesion of platelets on membrane surface during blood filtration. In membrane science, the experiment of platelet adhesion on membrane surface is usually employed to evaluate the hemocompatibility of a blood-contact membrane. In biomedical application, the adhesion of microbes on membrane surface often leads to the bacterial infection of patients and the deterioration of membrane materials. Therefore, the control of microbial infection is a very important issue in biomedical membrane separation.

Cross-References

- [Adhesion to Membrane Surfaces](#)
- [Adsorption onto Membrane Surfaces](#)
- [Biofouling](#)

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Bioartificial Liver

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Synonyms

Artificial liver; BAL; Biohybrid Artificial Liver (BAL)

Bioartificial Liver

Bioartificial liver is a system that consists of functional liver cells (hepatocytes) supported by an artificial cell culture environment. In particular it incorporates hepatocytes into a bioreactor, or biochemical reactor, in which cells are embedded and/or immobilized, cultured, and induced to perform all the liver-specific functions of the *in vivo* native liver: detoxification, biotransformation, excretion, synthesis, and modulation.

BALs have two major uses: in clinic as bioartificial liver support system (BALSS) to provide a short-term support for liver failure patients and in *in vitro* experimentation as a model system for therapeutic and toxicological studies.

BALs were developed as a promising approach for the treatment of patients with acute and fulminant hepatic failure. They don't offer a long-term nor a permanent substitute for an individual's liver. They support liver functions for a relatively short period of time and are intended to be used either as a bridge to a transplant or as a temporary support to allow the native or post-transplant liver to recover.

BALs with homogeneous and stable *in vivo*-like microenvironment are further employed as valid tools to investigate the basic biology of hepatic tissue development, to study liver diseases, to develop therapeutic strategies for drug-screening applications, to assess hepatic pathways of drug biotransformation, and to evaluate both

therapeutic and toxicological effects of various drugs and chemicals on hepatic metabolism (Salerno et al. 2013). The feasibility of BALs as good and achievable model systems for *in vitro* studies represents an alternative and/or complementary methods or procedure to *in vivo* animal experimentation. BALs as *in vitro* model systems allow the reduction of the number of laboratory animals and provide a faster and more cost-effective way of analysis. The use of human hepatocytes is the only system for a rapid, accurate, and highly specific evaluation of effects taking account of the species differences in liver response, substrate specificity, and enzyme induction between man and animals.

Critical issues in the design of a BAL are the configuration, the cell sourcing and density, the choice of the material for cell adhesion, the oxygenation and the gas exchanges, the mass transport of nutrients and catabolites, the scale-up, and the regulation and safety (Stevens et al. 2014). A successful BAL requires favorable culture conditions to maintain cell viability, functionality, and differentiation in the time. As liver cell sources, primary hepatocytes, either human or of xenogeneic derivation, human-immortalized hepatoma cell lines, hepatic progenitors, and intrahepatic or extrahepatic stem cells could be used.

Primary human hepatocytes represent the gold standard for their clinical safety and high liver-specific activity; however, their limited availability makes them unsuitable for clinical application and large clinical studies. Most systems are using xenogeneic cells of porcine origin which are more easily available; nonetheless the metabolic compatibility is not assured, and the transfer of xenogeneic virus and immunological reactions represent a potential risk. Human-immortalized hepatoma cell lines have the advantages of unlimited availability and good practicability, but they have low liver-specific activity and cancer-like cell metabolism. A large number of studies have utilized human liver-derived stem cells including fetal liver stem cells (hepatoblasts) and liver stem cells (oval cells) to generate primary hepatocytes; because of their rarity within the liver tissue, until today it is impossible to expand and differentiate

them to a sufficient cell mass. Other studies have induced extrahepatic stem cells, embryonic or adult stem cells, to differentiate into hepatocyte-like cells; although the pluripotent stem cells may be a suitable alternative to hepatocytes, their clinical use is limited by ethical concerns, for the first of them, and the risk for tumor development for both. A promising approach is in the use of induced pluripotent stem cells (iPSC) that are adult stem cells reprogrammed for their pluripotency by genetic manipulations (Lee and Cho 2012).

In an effort to recreate the interactions between parenchymal and non-parenchymal cells, hepatocytes have been co-cultured with several liver non-parenchymal cells such as endothelial cells, fibroblasts, stellate cells, and Kupffer cells, showing remarkable liver-like structure and functions.

Several types of BALs were developed by using cell suspensions, alginate beads, microcarriers, microcapsules, organoids, porous spheroids, collagen sandwich, and matrices.

To maintain hepatocyte functions and polarity, it's advantageous to mimic the matrix surrounding the hepatocytes in the sinusoid of the natural liver. To this purpose three-dimensional matrices or sandwiches configuration are the best environments for the long-term maintenance of viability, functionality, and differentiation state.

Polymeric membranes in flat sheet and in hollow fiber configurations are widely used as supporting materials for the design and development of BALs.

Membranes offer a substratum for adhesion of anchorage-dependent cells like the hepatocytes. Morphological characteristics (e.g., pore size, porosity, roughness) and physicochemical and mechanical properties of the membrane surface (e.g., wettability, surface free-energy parameters, Young's modulus) affect cell adhesion and the maintenance of cell viability, functionality, and differentiation in the time. Membranes with adequate molecular weight cutoff (MWCO) ranging from 70,000 to 100,000 Da represent a selective barrier for the compartmentalization of cells in nano- and microstructured environment ensuring immunoisolation and immunoprotection in allo-

xenogeneic implants and protection of cells from shear stress damages. Furthermore, the selective transport properties of membranes ensure a selective transport and an adequate mass transfer of molecules, nutrients, metabolic products, and endogenous and exogenous toxins as well as gas exchange from/to patient's blood or plasma and to/from the cell compartment.

The use of flat membrane bioreactors allows for control of the internal flow distribution and perfusion of all cells under a stable oxygen and nutrient gradient. The main drawbacks of a flat configuration are the difficulties to build a system with a sufficient cell density and an optimal ratio between the low surface area and the volume of the system. Most devices tested clinically employ hollow fiber membrane cartridges. In this configuration, the cells are compartmentalized, in the intralumen or in the extralumen of hollow fibers, and isolated from blood or plasma by the semi-permeable membrane with a proper molecular weight cutoff. However, the main drawbacks of a hollow fiber configuration concern inherent physical limitations including mass transport across the fiber wall and the hepatocyte mass, a limited total diffusion surface area, and an increased diffusion distance (Bao et al. 2011). The design of a successful BAL configuration could be optimized by modelling study in order to predict and verify the performance of the proposed configuration in terms of mass transport and cellular reaction rates.

Cross-References

- [Artificial Liver, Membrane Operations](#)
- [Bioartificial Liver Support System \(BLSS\)](#)
- [Bioartificial Organs and Tissue](#)
- [Bioartificial Organs, Membrane Operations of](#)
- [Biohybrid Artificial Liver \(BAL\)](#)
- [Biohybrid Artificial Liver \(BAL\) Systems](#)
- [Biohybrid Membrane Systems](#)
- [Membrane Artificial Organs](#)
- [Membrane Bioartificial Organs](#)
- [Membrane Bioreactors for Cell Growth](#)
- [Tissue Engineering, Membrane Operations of](#)

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Bioartificial Liver (BAL) Devices

► Bioartificial Liver Support System (BLSS)

Bioartificial Liver Support System (BLSS)

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Synonyms

Bioartificial liver (BAL) devices; Biohybrid artificial liver systems; Cell-based liver support systems; Extracorporeal BALs; Temporary liver support systems

Bioartificial Liver Support System (BLSS) is a bioartificial liver that supports liver functions. In contrast to purely artificial or nonbiological liver support systems in which detoxification process is based on the principle of adsorption and filtration, such as hemodialysis, hemoperfusion,

hemofiltration, and plasmapheresis, bioartificial devices incorporate a functional cell component. This latter is constituted by living and metabolically active hepatic cells, or hepatocytes, which are able to fully replace the specific functions of the *in vivo* native liver, including biotransformation, synthesis, and modulation in addition to detoxification and excretion. The liver is a vital organ with a wide range of functions in synthesis, detoxification, and regulation; hence, its failure constitutes a life-threatening condition that in most cases can be overcome by orthotopic liver transplantation. Owing the shortage of donor organs, a variety of alternative treatments was developed to replace some of the liver's function in case of liver failure. BLSSs are expected to increase spontaneous recovery or at least improve patient survival until transplantation is possible.

BLSSs employ hepatocytes as *implantable systems* or *extracorporeal systems* (De Bartolo and Bader 2002).

Implantable systems are tissue-engineered constructs proposed as potential permanent BLSSs for *in vivo* liver regeneration. They include hepatocytes on coated microcarrier beads, within microencapsulated gel droplets, within biodegradable polymeric membranes, or as spheroid hepatocyte aggregates. They however require a prolonged period for intraperitoneal engraftment and vascularization, and their potential to provide long-term hepatic support is still in a very preliminary and experimental phase and untested yet in clinical trials.

Extracorporeal systems provide metabolic support for a relatively short time and for the treatment of acute liver failure and patients for which the orthotopic liver transplantation is the only effective therapy. Such systems serve as a bridge to solid organ transplantation or as a temporary support to allow the native and/or post-transplant liver to regenerate and/or recover properly. They are not invasive to the body: a shunt veno-venous or arterio-venous is required to connect the patient to the device. Blood is removed from the vein and circulated through the device where it is processed by living liver cells and then returned to the patient using a dialysis-type procedure. In some devices the blood plasma

removed from the patient is separated from the other constituents by plasma separators before it circulates through the device. Extracorporeal BLSSs include hepatocytes in suspension as aggregates/spheroids or in adhesion to matrices and/or membranes into a bioreactor and may be recharged with fresh hepatocytes for both a continuous or intermittent use.

In the design of BAL devices, critical aspects have to be taken into account such as the cell source and density, the culture condition and the long-term maintenance of well-differentiated hepatocyte functions, the oxygenation and the mass transport, and the configuration and the scaling-up of the systems.

Several types of extracorporeal BLSSs with different configurations have been developed: in packed bed, flat membrane sheet, and hollow fiber membrane systems (Morelli et al. 2010; Stevens et al. 2014). The flat membrane bioreactors allow a high-density cell culture under sufficient oxygenated conditions; however, they present some disadvantages such as the complex up-scaling of large flat plates. Most of the BLSSs are composed of hollow fiber cartridges with different polymeric membranes. Hepatocytes are loaded in the extralumen space or injected into the lumen of the hollow fiber membranes. Some of them comprise more independent but interwoven capillary systems in a three-dimensional network for medium inflow, medium outflow, and oxygen/carbon dioxide exchange (Sauer and Gerlach 2002).

In both the implantable and extracorporeal systems, membranes serve as immunoprotective barriers against host defenses. Immunological rejection is reduced by means of membranes with molecular weight cutoff (MWCO) of 70,000–400,000 Da which act as immunologic barrier between the patient's blood and hepatocytes; thus, xenogeneic or allogeneic implants may be used without an immunosuppression therapy.

The selective transport properties of membranes ensure a selective transport and an adequate mass transfer of molecules, nutrients, metabolic products, endogenous and exogenous toxins, as well as gas exchange from/to the patient's blood or plasma and to/from the cell

compartment. Furthermore, membranes offer a large surface area for adhesion of anchorage-dependent cells like the hepatocytes, affecting the maintenance of cell viability, functionality, and differentiation in relation to membrane morphological characteristics (e.g., pore size, porosity, roughness) and physicochemical and mechanical properties (e.g., wettability, surface free energy parameters, Young's modulus).

Several extracorporeal systems have undergone extensive animal testing and are currently investigated in the early stages of human clinical trials (Zhao et al. 2012). A series of studies showed that BLSS devices reduced mortality in acute liver failure cases.

Cross-References

- ▶ [Artificial Liver, Membrane Operations](#)
- ▶ [Bioartificial Liver](#)
- ▶ [Bioartificial Organs and Tissue](#)
- ▶ [Bioartificial Organs, Membrane Operations of](#)
- ▶ [Biohybrid Artificial Liver \(BAL\)](#)
- ▶ [Biohybrid Artificial Liver \(BAL\) Systems](#)
- ▶ [Biohybrid Membrane Systems](#)
- ▶ [Membrane Artificial Organs](#)
- ▶ [Membrane Bioartificial Organs](#)
- ▶ [Membrane Bioreactors for Cell Growth](#)
- ▶ [Tissue Engineering, Membrane Operations of](#)

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Bioartificial Organs and Tissue

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Synonyms

Biofabrication; Engineered organs and tissue; Tissue engineering and regenerative medicine

Bioartificial Organs and Tissue

Artificial organs and tissues composed of cells supported by engineered extracellular matrices such as biomaterials or scaffolds in a suitable culture environment. These constructs are produced by applying principles from different established disciplines like engineering, chemistry, biochemistry, biology, and medicine, with the purpose to repair, replace, preserve, or improve the functions of damaged organs or tissues and as a possible alternative to the growing demand for their transplantation. Besides their *in vivo* application, human organs and tissue could be used as model systems for drug screening and testing and as valid tools to investigate the basic biology in *in vitro* research.

The new and functional living organs and tissue are fabricated using living cells, which are usually associated with a matrix or scaffold to guide the tissue and organ development, in a metabolic and physic microenvironment under tightly controlled conditions, such as bioreactors, for their maturation step.

The source of cells must be easily accessible, with a high proliferative capacity and ability to differentiate into the required cell type. Cells can be obtained from a fragment of adult tissue (primary cells) or from multipotent stem cells. They could be of autogeneic, allogeneic, or xenogeneic origin accordingly as they are from the same organism, from a donor of the same species, or from a different species, respectively. The

autologous primary cells have the advantage to avoid immuno-rejection and/or transmission of infective agents; however, only some of them present a high proliferative capacity. The use of embryonic stem cells (ESC) is very attractive though limited by ethical issues and their tumorigenic capacity. The isolation of adult (ASC) or mesenchymal (MSC) stem cells offers good alternative for their ability to activate and differentiate into multiple tissue cell types. Induced pluripotent stem cells (iPSC), which are ASC reprogrammed for their pluripotency by genetic manipulations, have been recently described as a new source of cells to regenerate tissues.

Biomaterials and scaffolds provide the appropriate biochemical and biomechanical cues for cell attachment and proliferation by mimicking the extracellular matrix (ECM) for cells. Due to their interaction with living cells, they must be biocompatible, nontoxic, and pharmacologically inert. These biomaterials can be permanent or biodegradable and made of synthetic or natural polymers or a composite network of both. The natural biological ECM, in addition to mechanical integrity, contributes in the development, maintenance, and regeneration of tissues, and it is itself a dynamic structure actively remodeled by the cells with which it interacts. Taking into account this consideration, the design characteristics of biomaterials and scaffolds are major challenges for materials scientists and should be considered at a molecular chemical level. Thus, new strategies are focusing on the development of interactive biomaterials that, by cell-material interactions, are able to activate, stimulate, and trigger cellular specific responses like cell proliferation and/or differentiation of embryonic and/or progenitor cells, driving the self-tissue formation and organization into a 3D construct. ECM-specific molecular structures or specific receptors and anchorage sites, as well as growth and differentiation factors, could be incorporated into cell support components to more closely replicate the native environment of the cells (De Bartolo et al. 2012). Composites of synthetic or natural polymers with bioactive ceramics or certain glasses can be designed to yield materials with a wide range of strengths and porosities for the engineering of hard tissues (Furth and Atala 2014).

After the cell seeding onto scaffolds, the maturation of an organ- or tissue-engineered construct takes place in bioreactors. Such systems facilitate the reproducible growth and production of bioartificial constructs under tightly controlled conditions, overcoming the limited seeding efficiency and poor transport of nutrients, oxygen, and wastes of the static cell culture conditions. The control of mass transport and gas exchange is particularly required for the development of highly perfused and oxygenated bioartificial organs, such as the liver and kidney. On the contrary, low oxygen tension is essential to improve the functions of engineered cartilage or to mimic the normal micro-environment or “niche” for stem cells. Furthermore, bioreactors may be used to enhance tissue formation through mechanical stimulation of the bone, cartilage, blood vessels, and skeletal and cardiac muscles. In particular, a pulsatile flow is helpful for the maturation of blood vessels, while a mechanical stretch strengthens engineered muscles (Furth and Atala 2014).

Scaffold-based tissue engineering has led to significant results in the reconstruction of various tissues. Small parts of bioartificial tissues (i.e., skin, cartilage, bone, blood vessels, corneas, urinary bladder, left mainstem bronchus, and trachea) have been successfully developed in experimental animals and approved either for human use or in clinical trials (Vacanti 2010; de Mel et al. 2012).

Currently, tissue engineering only offers the possibility of recovering lost function, while the formation of whole organs and tissues similar to the natural ones is still not a reality because of the difficulty in providing vascularization, innervation, and the same signals of the extracellular matrix.

Recently, novel approaches that do not rely on artificial scaffolds have been pursued. The most promising ones utilize matrices of decellularized organs or bioprinting-based technologies. The xenogeneic whole-organ *decellularization* allows the production of complex three-dimensional extracellular matrix bioscaffolds of the entire organ with preservation of the intrinsic vascular network. These bioscaffolds can then be recellularized by autologous cells to create

potentially functional organ constructs. With this strategy, it has been possible to obtain organs such as the heart, liver, trachea, and lungs (He and Callanan 2013). The so-called organ printing is based on multicellular self-assembly by a computer-aided bioprinting technology. 3D printers combined with image-processing software, operating with *bioink* particles of spheroidal cell aggregates and *biopaper* of biocompatible ECM hydrogels, are able to form and build complex 3D living structures with complete control of the internal structure, including a vascular tree (Marga et al. 2012).

Cross-References

- ▶ [Bioartificial Liver](#)
- ▶ [Bioartificial Liver Support System \(BLSS\)](#)
- ▶ [Bioartificial Organs, Membrane Operations of](#)
- ▶ [Biodegradable Polymer for Membranes](#)
- ▶ [Biohybrid Membrane Systems](#)
- ▶ [Membrane Artificial Organs](#)
- ▶ [Membrane Bioartificial Organs](#)
- ▶ [Membrane Bioreactors for Cell Growth](#)
- ▶ [Tissue Engineering, Membrane Operations of](#)

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Bioartificial Organs, Membrane Operations of

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Synonyms

Biohybrid membrane systems; Engineered organs; Organotypic membrane systems; Regenerative medicine

Bioartificial Organs, Membrane Operations

Artificial organs realized by taking advantage of membrane technology and operations. They consist of functional cells supported by polymeric membranes as scaffold, in a suitable culture environment in which cells are maintained and induced to perform all the specific functions of the *in vivo* native organ. In most cases they incorporate cells into membrane bioreactors.

Organ level tissue engineering requires a biomimetic microenvironment that provides substrates for cell maintenance and proliferation and signaling cues directing morphogenesis and cell differentiation toward tissue-specific structures and phenotype. The choice of biomaterials with high biostability and biocompatibility and with specific physicochemical, mechanical, and morphological properties on the basis of the targeted tissues or organs is crucial for successful bioartificial constructs.

Progress in membrane technology and in membrane operations in understanding and controlling micro- and nano-properties and selectivity in transport phenomena currently offer new interesting opportunities for the design of bioartificial organs. Membranes in flat sheet and in hollow fiber configurations serve to house cells, supporting their growth and adhesion and directing their reorganization in a three-dimensional architecture.

Moreover membranes, exposing cells to an adequate perfusion and oxygenation, are able to guide cellular differentiation and functions (Salerno et al. 2013a).

The first concept of membrane-based bioartificial organs was based on the development of implants containing living xenogeneic or allogeneic cells enclosed and/or encapsulated in a selective membrane barrier for cell transplantation. In such compartmentalized system, membranes act as a selective barrier for immune isolation of cells. They admit the unhindered passage of oxygen and small molecules required for cell metabolism and the release of bioactive components to the host. In particular, the selective transport properties of membranes ensure the transport and an adequate mass transfer of nutrients, metabolic products, growth factors, endogenous and exogenous toxins as well as gas exchange. In the meantime, membranes with adequate molecular weight cutoff (MWCO) ranging from 70,000 to 100,000 Da restrict the passage of larger cytotoxic agents of the immune defense system, allowing the immune isolation and immune protection of cells in allogeneic and xenogeneic implants. The use of membranes as a selective barrier eliminates the need of chronic immune suppression in the host and allows the use of allogeneic and xenogeneic cells, thus avoiding the cell-sourcing constraints. Furthermore, the compartmentalization of cells in nano- and micro-structured environment ensures and protects cells from shear stress damages in membrane bioreactors (Drioli and De Bartolo 2006). Recent advances in mesenchymal stem cell biology and in their expansion and differentiation have made possible the use of autologous cell source to avoid the immuno rejection drawback.

In bioartificial organs, polymeric membranes not only act as selective and immune protective barriers, but they also play a crucial role in cell adhesion and cell interaction mimicking the extracellular matrix (ECM) with which cells interact. A proper cell-material interaction could trigger cell growth, migration, proliferation, differentiation, and functional activation, thus allowing the organization of cells in a three-dimensional architecture and the maintenance of cell viability and

functionality. At the same time, an inappropriate cell-material interaction could trigger programmed cell death or apoptosis.

New biofabrication approaches to create and develop complex organotypic and organomimetic systems reckon with molecular, architectural, and biophysical basis of tissue principles which are tightly related to developmental biology and morphogenesis. Recent advances in the molecular cell biology of morphogenesis, as well as in stem cell biology, will aid in the design principles and architecture for tissue engineering and regeneration (Ingber 2014). Organs are made of tissues and tissues are made of cells. To make and tailor bioartificial organs is necessary to start from tissue engineering and, therefore, from cell-material interactions.

The choice of ideal scaffold materials, optimum cell source, and well-defined tissue culture conditions is required for the realization of safe and confident bioartificial substitutes for clinical application.

Membranes are eligible scaffolds for tissue engineering and bioartificial organs. The majority of membranes for the realization of organ membrane systems are manufactured from homogeneous polymer solutions by phase inversion. This technique is a very versatile process for the synthesis of membranes from different polymers, also biodegradable, and with a wide variety of modulated morphological, physicochemical, mechanical, and transport properties depending on the target bioartificial organ.

Porous membranes with specific *pore size* and *porosity* influence cell adhesion and the transport and/or diffusion of nutrients and metabolites, to and from cells. Morphological and physicochemical surface properties, such as *roughness*, *wettability*, and *free energy parameters*, affect cell adhesion and consequently the cell shape either indirectly, by controlling the adsorption of proteins, or directly, by guiding cell spreading and cytoskeleton rearrangements. *Topographical cues*, including grooves, ridges, wells, and nodes, drive the cell orientation and migration and the three-dimensional architecture of the growing bioartificial organ. *Mechanical properties* play in control of cell growth, differentiation,

motility, and apoptosis. The signals that are actually responsible for dictating tissue pattern are often mechanical in nature, such as compression on the bone, shear stress on blood vessels, and tension on muscles. The choice of materials with specific mechanical properties is strictly related to the target tissue or organs: the bone (hard tissues) necessitates stiff matrices; tendons, ligaments, skin, fibrous tissues, muscles, nerves, and blood vessels (soft tissues) need more elastic and flexible scaffolds. Since both embryogenesis and mesenchymal differentiation toward the formation of new organ rudiments take place under mechanical tension and compression, differentiation of embryonic and mesenchymal stem cells is strongly influenced by substrate stiffness. On polymeric membranes, an enhanced tensile modulus and strength and a high porosity are able to promote capillary development by endothelial cells, thus favoring the vascularization in organotypic membrane systems (Salerno et al. 2011).

To tailor the material bioactivity and to more closely replicate the native and natural microenvironment of the cells, membranes and biomaterials could be modified by incorporating biomolecules and/or ECM-specific molecular structures. They could also include structural units for the targeted controlled release of bioactive molecules as growth factors or cytokines to be released at the right time and at the right place and to mimic natural signaling pathway. Moreover, the design of *biodegradable membranes* with a programmed and predictable biodegradation rate consistent with the tissue formation rate is useful for implantable bioartificial constructs. The research strategies for the next 20 years will focus on the implantation of bioartificial tissues and the induction of the *in situ* regeneration and self-repairing of damaged organs and tissues (De Bartolo et al. 2012).

Although the engineering of fully functional bioartificial organs for transplantation is not yet a reality for the difficulty in providing vascularization and innervation, bioartificial tissues with increasing complexity reach clinical application nowadays. Advances in biomaterials and in stem cell biology have made possible the realization of

tissues and organotypic bioartificial systems for clinical as well as basic research applications. Membrane systems supporting and stimulating cell differentiation and proliferation have been involved in the biofabrication of active substitutes in static and dynamic conditions (Salerno et al. 2013a, b). The dynamic culture models such as the *membrane bioreactors* may simulate the *in vivo* complex physiological environment through the fluid dynamics modulation and the selective membrane transport, ensuring an adequate mass transfer of nutrients and metabolites. In such microenvironment a constant turnover of tissue culture medium augments the gas and nutrient exchanges, which together with the complete fluid dynamics control ensures the long-term maintenance of cell viability and functions. Membrane bioartificial organs could be used as implantable or extracorporeal devices for tissue loss or organ failure and for the designing of *in vitro* model systems for drug screening and diagnostic applications. Examples of membrane bioartificial organs are the membrane bioartificial liver and the bioartificial liver support systems.

Cross-References

- ▶ [Bioartificial Liver](#)
- ▶ [Bioartificial Liver Support System \(BLSS\)](#)
- ▶ [Bioartificial Organs and Tissue](#)
- ▶ [Biodegradable Polymer for Membranes](#)
- ▶ [Biohybrid Membrane Systems](#)
- ▶ [Membrane Artificial Organs](#)
- ▶ [Membrane Bioartificial Organs](#)
- ▶ [Tissue Engineering, Membrane Operations of](#)

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Bioartificial Synthetic Membrane

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Synonyms

[Artificial biological membrane](#); [Biological and synthetic membrane](#); [Synthetic biomembrane](#)

Introduction

Bioartificial synthetic membrane is a synthetic enclosing or separating membrane that functions as a selectively semipermeable barrier of artificial organs such as artificial livers, artificial kidneys/dialyzers, and artificial lungs/blood oxygenators. Bioartificial synthetic membrane can separate the contents (e.g., cells) and components of the recipient's immune system (Nyberg et al. 2003). The importance of a bioartificial synthetic membrane is suggested by the rapid influx of ultrafiltrate components and the reservation of functional cells (e.g., human primary renal proximal tubule cells of bioartificial kidneys), with the inhibition of undesired back diffusion into the recipient's system (Ni et al. 2010).

Generally, bioartificial synthetic membranes that are in contact with biological fluids should prevent any type of infection and immune

response, thrombus formation, and other biological response that could affect the properties of the fluid (Stamatialis et al. 2008). The approaches to the development of biocompatible membranes include three categories: (1) optimization of synthetic polymer, (2) modification of material surface, and (3) construction of biomimetic membrane surfaces (Kawakami 2008). So far, a variety of materials have been used for bioartificial synthetic membranes, including polymethyl methacrylate, polydimethylsiloxane, polysulfone, polyethersulfone, poly(ethylene oxide), and poly(vinyl alcohol). Alternatively, membrane surface properties can be modified to suppress immune response, and prevalent methods are comprised of plasma etching, corona discharge, UV irradiation, and covalent attachment (Yoshida et al. 2006).

Nondegradability is an important factor for bioartificial synthetic membranes. Unexpected swelling and leaching can result in reduced fracture strength and elastic modulus of the material, leading to static fatigue or crazing (Stamatialis et al. 2008).

It is very important that bioartificial synthetic membranes can have identical functions as the organs, which is closely related with membrane structure. The structure parameters of membranes generally include thickness, pore size, porosity, and so on. For instance, in artificial kidneys, the pore sizes should be well controlled in order to prevent leakage of useful proteins in blood such as blood corpuscles and albumin (molecular weight 69,000 Da) while removing harmful substances (Kawakami 2008). Microdomain structure is also important for interaction of membranes with seeded cells. Differentiated epithelia of human primary renal proximal tubule cells have been found on the optimal membrane materials with/without coatings (Ni et al. 2010), and the concept of developing asymmetric membranes is suggested for bioartificial synthetic membranes.

Cross-References

► [Biological Membrane](#)

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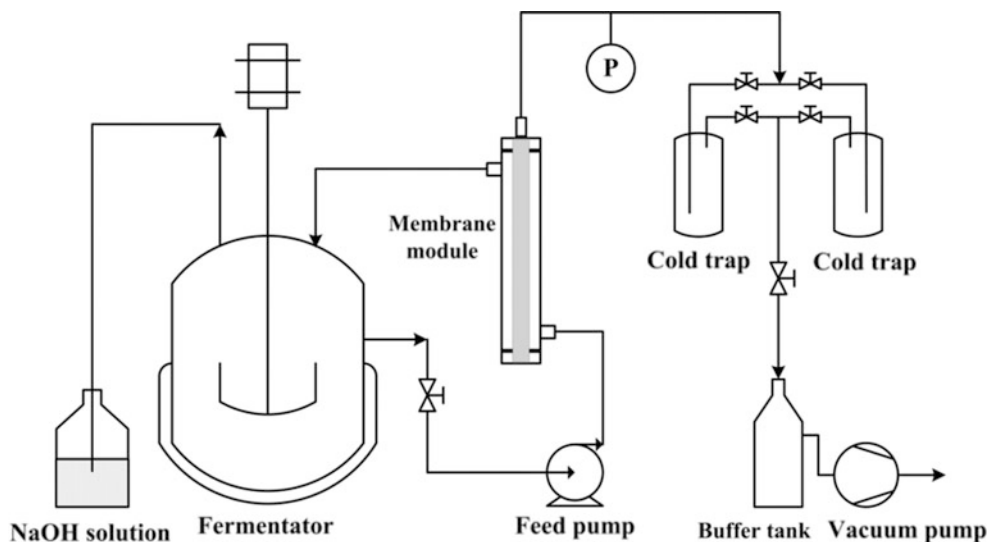
Biobutanol Recovery from Biomass Fermentation Broth

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Biobutanol recovery from biomass acetone-butanol-ethanol (ABE) fermentation broth by pervaporation is a process that couples ABE fermentation with in situ pervaporation recovery acetone, butanol, and ethanol from fermentation broth.

During the past decade, there has been an increasing interest for the production of biofuels from renewable resources because of growing concerns about global warming and increasing consumption of crude oil. Butanol, as compared to ethanol, is less volatile and explosive, contains more energy, and can easily mix with gasoline in any proportion. In addition, butanol can be used directly or blended with gasoline or diesel without any vehicle retrofit, since the air to fuel ratio and the energy content of butanol are close to gasoline (Qureshi and Ezeji 2008). Biobutanol is produced



Biobutanol Recovery from Biomass Fermentation Broth, Fig. 1 ABE fermentation-pervaporation-coupled process

from renewable resources (biomass) by acetone butanol ethanol (ABE) fermentation process. However, usually the maximum concentration of total solvents (ABE) do not exceed 20 g/L due to the end-product inhibition on microbes, resulting in high energy cost to recover ABE from the dilute fermentation broth by distillation. Therefore, several in situ product-removal technologies, such as adsorption, gas stripping, liquid-liquid extraction, perstraction, pervaporation, and reverse osmosis, have been developed. These technologies could be coupled with ABE fermentation process to reduce the effect of product inhibition and improve the sugar utilization and solvent productivity (García et al. 2011).

Pervaporation (PV) is a membrane process for liquid separation, in which a polymeric or inorganic membrane usually serves the separating barrier. The application of PV for butanol recovery from fermentation broth is based on the selective permeation of organic compounds through the membrane when the nature of the membrane is hydrophobic. PV is especially effective for the system in which the concentration of the targeted species is low; for instance, the butanol content in the fermentation broth is very low. Furthermore,

the pervaporation process is energy efficient and it is harmless to the fermentation broth.

PV membranes can be made from either polymeric or inorganic materials, even both of them (Qureshi and Blaschek 1999). The polymeric pervaporation membranes for extracting butanol from fermentation broth include polydimethylsiloxane (PDMS) membranes, poly [1-(trimethylsilyl)-1-propyne] (PTMSP) membranes, poly(ether block amide) (PEBA) membranes, liquid membranes, other modified polymer membranes, as well as porous polypropylene (PP) membranes and polytetrafluoroethylene (PTFE) membranes. Among them, the commonly used PDMS membranes with good selectivity and stability are regarded as the most potential PV membranes for butanol recovery application. The typical inorganic membrane for PV is hydrophobic zeolite membrane, such as ZSM-5 and silicalite-1 membrane. The process of biobutanol recovery from biomass ABE fermentation broth by pervaporation is also called ABE fermentation-pervaporation-coupled process; its conventional flow chart is shown in Fig. 1 (Liu et al. 2011). A pervaporation membrane module is connected to the fermentor, and the ABE solvent

can be selectively and continuously removed from the fermentation broth and then concentrated in the membrane downstream side. As result, the ABE concentration in the broth is kept at low level to facilitate the continuous fermentation process as well as enhance the solvent productivity. In addition, a microfiltration/ultrafiltration unit can be alternatively installed before the pervaporation module, in order to retain microbes and avoid the biofouling of pervaporation membranes.

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Biocatalyst Recycling by Membrane Operations

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Owing to current industrial demands for environmentally friendly solutions and cleaner

technologies, the end-of-life purification techniques that were applied for the product streams are being replaced with integrated process solutions in closed systems. Exhibiting high activities and selectivity difficult to achieve with chemical catalysts, biocatalysts have been regarded as ideal catalysts. The widespread use of biocatalysts in industrial processes is however largely impeded by their unfavorably high economic costs. The recycling of the expensive biocatalysts is therefore an important goal in applied biocatalysis, which would in turn promote the development of industrial enzyme-mediated processes.

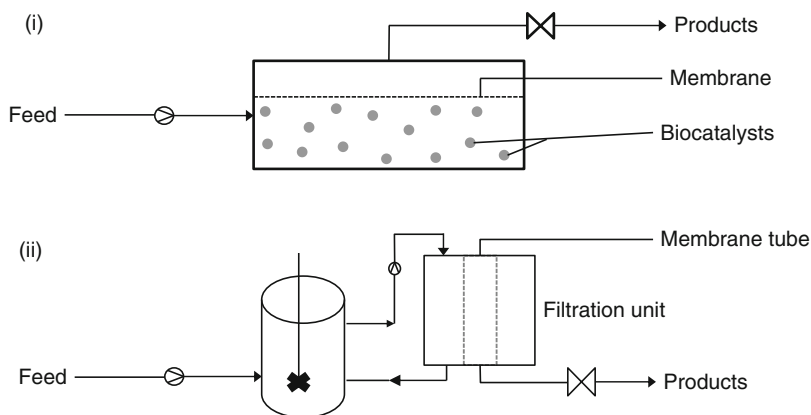
Membrane filtration is an essential tool in the biotechnological industry and appears to be particularly useful for the purification and concentration of proteins. Membrane technologies could therefore be applied to achieve this goal of biocatalyst recycling. The application of membrane technologies in the field of biocatalyst (i.e., enzyme and whole cell)-mediated conversions could aid in achieving process simplification, as well as facilitating a recycling and reuse of the biocatalysts, and in reducing the process costs and could be a separation step for the components of the process effluent stream. The membrane retention and enzyme recycling methods described here are different from systems where the enzymes are immobilized on or entrapped in a membrane. The use of membrane technologies for biocatalyst recycling in biochemical processes however depends on a number of important features of the membranes employed.

Membrane processes can be differentiated on the basis of the size and geometry of the particles which are aimed to be retained (and recycled), for example, the use of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) techniques. With their ability to retain the biocatalytic entities and macromolecules (i.e., whole cells and enzymes) with dimensions between 8–800 and 0.5–8 nm, UF and NF membranes are most widely applied for biocatalyst recycling (Dijkstra et al. 2002).

Most UF and NF membranes are asymmetric membranes, with the pore sizes on the solute side

Biocatalyst Recycling by Membrane Operations,

Fig. 1 Biocatalyst membrane recycling schemes via (i) dead-end filtration and (ii) Cross-flow (loop) techniques



of the membrane smaller than those on the permeate side, which in turn largely prevents membrane clogging. The membrane stability under different operational conditions is also a very important factor which must be considered, since it indicates the potential biocatalytic processes which the selected membranes can be suitably applied for. This includes a consideration of the various possible interactions that the different reacting components and intermediates in the conversion process could have with the membrane surface. Unfortunately, data concerning such aspects must still largely be obtained by empirical investigations, since extensive data for most membranes is still lacking and not widely available.

The molecular weight cutoff (MWCO), which is defined as the molecular weight at which 90 % of the solutes are retained by the membrane, is usually used as the main quantitative criterion for the characterization of the membrane retention. It should however be remembered that the pore size distribution, charge effects, hydrophilicity, hydrophobicity, and polarity (of the solvents) can also greatly influence the permeability and functioning of the membrane (Dijkstra et al. 2002). In addition, especially in the case of biocatalyst recycling, the molecular shape and characteristics are important factors when considering biocatalyst retention using membranes. For example, globular proteins are more efficiently retained by membranes compared to the retention of flexible

polymers having elongated chains (Dijkstra et al. 2002).

Two major schemes can be applied for the recycling of biocatalysts using membrane operations. These are the use of (i) dead-end filtration and (ii) cross-flow (loop) filtration as shown in Fig. 1.

With the dead-end filtration technique, the biocatalyst is isolated in the reactor and is retained using UF or NF membranes. The reactants are continuously pumped into the reactor with the product and unreacted substrates permeating through the membrane for forward processing. However, the accumulation of the catalyst (i.e., concentration polarization) near the membrane surface can occur using this method. Using the cross-flow technique, the potential catalyst concentration polarization issue can be prevented, since the reaction solution is continuously circulated through the reactor. This ensures that the membrane is continuously swept clean by the fluid cross-flow going past the surface which then minimizes the enzyme build up while allowing the products and unreacted materials pass laterally across the membrane.

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Biocatalytic and Biochemical Membrane Reactor

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Synonyms

Biochemical membrane reactors

A biocatalytic membrane reactor (also referred to as a biochemical membrane reactor) is a system or device that combines and utilizes the separation capabilities of membranes and the catalytic activities of whole cell or enzyme biocatalysts in one unit to facilitate the biochemical conversion of substrates into desired products and the selective removal of the products in a single process unit. The removal of the product components from the reaction site could in turn improve the conversion of the substrates by favoring the product formation reaction and is thus useful for reactions that are thermodynamically unfavorable or are product inhibited. The separation of permeable solutes can be achieved from the reaction mixture by the action of a driving force that is applied across the membrane. As a result of coupling the conversion reaction with separation, lower operating costs could therefore be achievable with this type of reactor design compared to the use of multiple reaction and product separation methods.

The complete retention of the biocatalyst within the reactor system is the most important requirement for the successful continuous operation of biocatalytic membrane reactors. Ultrafiltration membranes with a pore size distribution range (nominal molecular weight cutoff, NMWCO, of 500–100 kDa) are the most adequate for the retention of a majority of native or

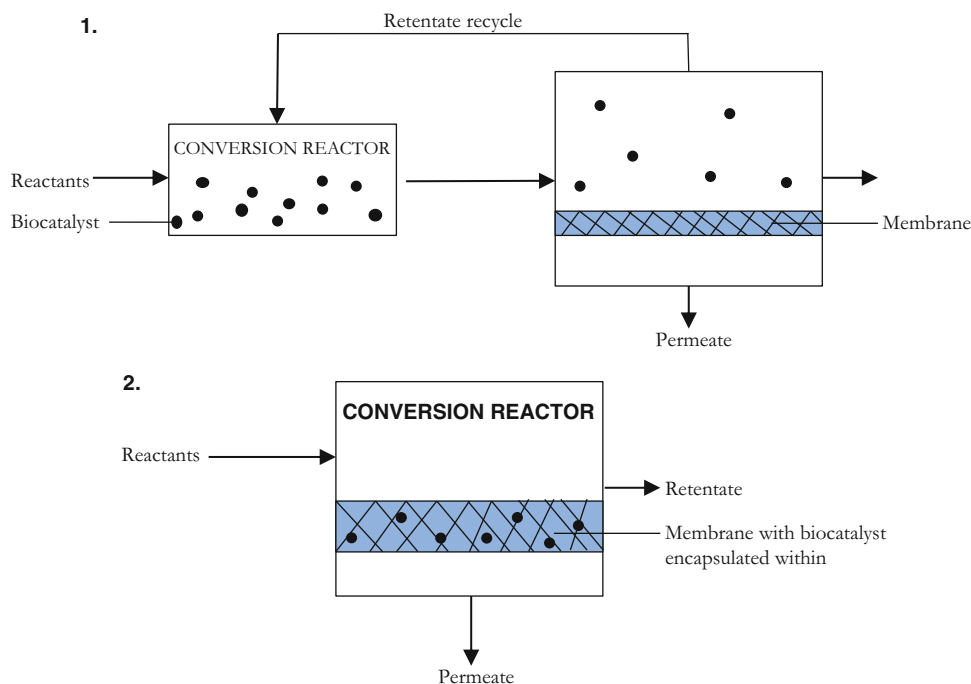
modified enzymes (10–100 kDa) (Prazeres and Cabral 1994).

The biocatalyst is usually present in the reactor system in two forms: free or immobilized at the membrane surface or inside the membrane matrix pores. If the biocatalyst (i.e., enzyme) is present in its free form, its immobilization can be achieved by confining the enzyme to one side of the membrane unit. This can be facilitated by size exclusion, electrostatic repulsion, or enlargement via chemical or physical immobilization techniques onto an intermediate support (i.e., inert proteins and gels). As for the direct immobilization of the biocatalyst onto the membrane, this can be achieved by chemical binding, physical adsorption, or electrostatic attraction.

Ideally the products resulting from the biocatalytic process should permeate through the membrane pores either via a concentration gradient-induced diffusion or a pressure gradient-induced convection. This would in turn facilitate a continuous removal of products from the reaction media, a process which has been considered to be essential for biocatalytic membrane reactor concepts. The selection of the membrane unit to be incorporated into the reactor system must take into account the respective sizes of the enzymes, substrates, and products, as well as the chemical characteristics of the reacting species and of the membrane. Here, the solute rejection coefficient is an important membrane selection parameter for the reactors and should be zero and one for the products and the biocatalysts, respectively (Prazeres and Cabral 1994). This would allow for the product/coproduct permeation through the membrane and a complete retention of the biocatalysts inside the reaction system.

The configurations of biocatalytic membrane reactors can be categorized into two main types (Fig. 1) (Giorno and Drioli 2000):

1. The biocatalyst (i.e., whole cells, enzymes, or antibodies) are used in solution for the conversion of the substrate to the desired products in a reactor and further transported to a reaction vessel containing a selected membrane where



Biocatalytic and Biochemical Membrane Reactor, Fig. 1 Main configuration types for biocatalytic membrane reactors; (1) Conversion reactor combined with a

membrane unit, (2) Submerged membrane reactor with the membrane functioning as a catalytic and separation unit (Adapted from Giorno and Drioli 2000)

the biocatalysts (and unreacted substrates) can be recycled back to the conversion reactor, with the permeate selectively extracted from the reaction stream. Here, the biocatalytic membrane reactor system might consist of a conventional stirred tank reactor combined with a membrane-separation unit.

- The biocatalyst constituents are immobilized within the membrane of the matrix. Here, the membrane acts as a support system for the biocatalyst as well as a separation unit.

The membrane units of the membrane reactor system can comprise of membranes which have a flat sheet shape (i.e., arranged in a plate and frame module or a spiral wound module) or tubular (assembled in a tube and shell module) (Giorno and Drioli 2000).

Advantages and disadvantages of biocatalytic membrane reactors (Prazeres and Cabral 1994):

Advantages	Disadvantages
Possibility of developing continuous conversion processes	Unfavorable adsorption and enzyme poisoning issues
Improved control of reaction systems	Enzyme deactivation due to shear-related effects
Increased productivities	Concentration polarization
Contribute in a favorable shift of the reaction toward product side	Likely product/substrate inhibition at the membrane surface
Better conversion rates in product-inhibited reactions	Membrane fouling
Good product enrichment and concentration in process stream	Enzyme leakage
Facilitates control of the molecular weight of hydrolyzates	
Allows the conducting of multiphase reactions, without emulsification issues	
Useful refined research tool for studying enzyme mechanisms	

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Biocatalytic Hollow Fiber Membrane Reactor

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Biocatalytic hollow fiber membrane reactor refers to biological or enzyme-mediated reactor systems which employ the use of hollow fiber membranes as a support for enzyme or cellular immobilization, biocatalyst, and substrate recycling and as a means of concentrating selected reaction streams. A hollow fiber membrane is a tubular-structured semipermeable membrane with a center called “the lumen” having diameters in the size ranges 50–6000 μm as seen in Fig. 1 (Bunch 1988). Such small diameters facilitate a large membrane area (i.e., active surface) per unit volume for the bioreactor system, as well as enable the operation of the processes at higher pressures (Katoh and Fumitake 2009).

Where the semipermeable membrane structure continues to the outer surface of the fiber, the matrix is considered to be uniform, and this type of fiber is termed isotropic. In cases where the semipermeable membrane only has a thickness of 0.1–0.5 μm and is surrounded by a more open structure, the fibers are called anisotropic (Bunch 1988). Although the open spongy structure of anisotropic fibers is often larger than most used enzymes and microbes that may be employed in bioreactors, before such biocatalysts can gain entrance to the matrix, the pores on the outer surface (shell side) of the hollow fiber need to be more than 1 μm in diameter (Bunch 1988). The outer pore sizes have however been noticed to vary from different manufacturers, even when comparing anisotropic hollow fibers having different filtration characteristics from the same company.

Configuration and Operation of Biocatalytic Hollow Fiber Membrane Reactors

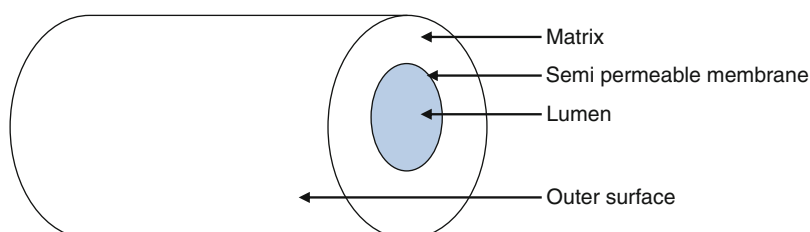
The hollow fiber membrane modules can be either integrated into the biocatalytic reactor system in an external loop or incorporated directly into the bioreactor as a submerged membrane unit. In either case surface shear and/or backflushing is used to limit the membrane fouling (Fane, et al. 2002).

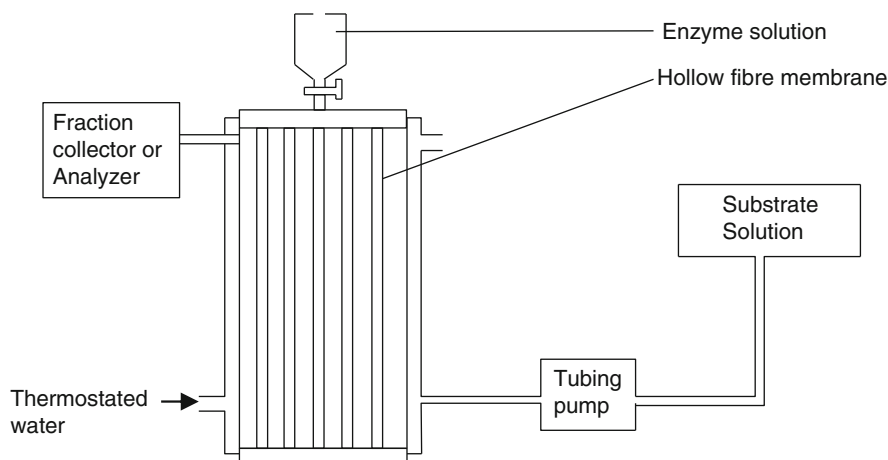
The immobilization and operation of the biocatalysts in the hollow fiber membrane reactors can be mainly classified into two categories (Hiromi and Norio 1984):

1. The biocatalyst (enzyme) solution may be introduced to the outside of the hollow fiber or to the inner lumen, with the substrate

Biocatalytic Hollow Fiber Membrane Reactor,

Fig. 1 Basic structure of a hollow fiber (Adapted from Bunch 1988)





Biocatalytic Hollow Fiber Membrane Reactor, Fig. 2 Schematic drawing of a hollow fiber membrane enzyme reactor (Hiromi and Norio 1984)

solution flowing on the opposite side of the membrane to the enzyme. The substrate molecules permeate the membrane and react with the entrapped enzyme. The product then diffuses back through the membrane to the substrate solution from where it can be further recovered (Fig. 2).

2. The enzyme solution is ultrafiltered into the porous region of an asymmetric hollow fiber membrane, or the hollow fiber is dipped into the enzyme solution so as to result in the absorption of the enzyme molecules into the spongy lumen. The substrate is then pumped into the reactor as previously highlighted. After the enzymatic conversion, the product permeates through the membrane into the lumen where it is collected.

Since the biocatalyst entrapment is not chemically modified, the kinetic behavior of enzymes in hollow fiber membrane bioreactors could be expected to be similar to those exhibited by free enzymes. However, with hollow fiber reactors in the first category, the substrate permeation into the membrane has been determined to be the rate-limiting step (Hiromi and Norio 1984). The rate of the biocatalytic reaction therefore tends not to

achieve maximum levels when compared to the same concentration range using free enzymes. This is since the actual substrate concentration in the “enzyme solution chamber” is always lower than the bulk substrate concentration as a result of the enzyme reaction.

Furthermore, the dependence of the catalytic rate on process temperature and pH for hollow fiber biocatalytic reactors are different from that of the free enzyme (Hiromi and Norio 1984).

Regardless of the mode of operation used, bioreactors can be run in parallel or in series. With the use of a parallel setup, defective reactors can easily be replaced without impacting the operation of the other reactors while the use of a series configuration could aid the use of different biocatalysts when sequential product transformations are required.

The control of the reaction temperature of the biocatalytic hollow fiber membrane reactors can be obtained by the use of a jacket with thermostated water circulated at the desired reaction temperature (as seen in Fig. 2), by the immersion of the bioreactor system in a temperature-controlled water bath or by containment in a constant temperature cabinet.

Advantages and Limitations with the Use of Hollow Fiber Biocatalytic Membrane Reactors

Potential Merits with the Use of Hollow Fiber Biocatalytic Membrane Reactors (Bunch 1988; Luther et al. 1992)

1. The possibility of immobilizing and using biocatalyst in one step
2. Potential regeneration of the biocatalyst
3. No enzyme losses or washout
4. Ease of process scale-up
5. Ease of reactor cleaning with lower sterilization requirements
6. Possibility for high volumetric productivity
7. Ease of enzyme dosing
8. Achieve homogenous catalysis with no limitation of substance transport
9. Lower bioreactor capital cost
10. Lower operational costs due to reduced need for further purification and immobilization
11. Less susceptible to contamination

Limitations with the Use of Hollow Fiber Biocatalytic Membrane Reactors (Bunch 1988)

1. The bioreactors usually require a particulate free media.
2. The use of organic solvents is usually restricted.
3. Fiber rupture.
4. Decreased stability of the biocatalysts.
5. Difficulty in recycling the membrane fibers.

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Biocatalytic Membrane

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Synonyms

Immobilization of enzymes

Biocatalytic membranes refer to the membrane systems which have been equipped to carry out biochemical reaction function via the integration of biocatalysts (i.e., whole cells and enzymes) on/within the membrane structure. Ultrafiltration, microfiltration, and dialysis membranes have been adapted to make biocatalytic membranes. These membranes can be activated so as to provide suitable conditions where the intended biocatalyst components can be coupled to it by physicochemical techniques.

The biocatalytic membranes are used in the bioreactor as a carrier or matrix for enzyme immobilization as well as a selective barrier. Such reactors are referred to as biocatalytic membrane reactors (BMRs). One of the interesting advantages of using biocatalytic membrane is the occurring of transport phenomena that are governed by convective flows. Convective flows are indeed the combination of diffusive and advective flows and thus are more intense than only diffusive flows. In case of conventional supports/carriers such as beads, only such diffusive flows govern the process rendering it less effective. In biocatalytic membrane there is generally a close contact between the membrane and the enzymes as a result of the enzyme immobilization. Such a close contact affects the properties of the immobilized enzymes depending both on the properties of the membrane and the enzyme itself. One of these enzyme properties, the pH optimum,

often shifts after the immobilization on a certain carrier. Predicting the direction of such a shift in pH optimum is sometimes possible by looking at the charge of the used carrier, but such predictions are uncertain and merely indicative. Furthermore, enzyme properties are affected by the used immobilization technique, which also will significantly determine the performance of the system. Therefore, the choice of immobilization technique and membrane is vital to obtain a high performing system, and both need attention when designing a new biocatalytic membrane system (Jochems et al. 2011).

Various immobilization techniques or chemistries are available for the manufacturing of biocatalytic membranes or for immobilizing enzymes on the membrane which can be realized via adsorption, entrapment, and chemical coupling methods such as cross-linking or covalent immobilization. The immobilization of the biocatalysts can also be achieved via gelation techniques. With the gelation method, the biocatalyst is immobilized in the gel layer formed during ultrafiltration due to the concentration polarization phenomenon (Gekas 1986).

For the preparation of the entrapped biocatalytic membranes, the phase inversion technique is usually applied. Here, the biocatalysts are introduced to the casting solution so as to contain the enzymes or whole cells in the polymeric structure of the resulting membrane. The use of the encapsulation method, which is similar to the entrapment method, has the biocatalyst contained in the liquid membranes formed via the emulsification of aqueous enzymatic phase with the organic membrane phase.

The cross-linking with bifunctional agents, i.e., glutaraldehyde (which is the most common bifunctional agent), is the simplest demonstrated method for the chemical immobilization of biocatalyst on membrane systems. Here, the biocatalysts initially need to be adsorbed onto/within the membrane structure. The formation of covalent bonds within the free amino groups in the enzyme molecule can then be achieved without any presence of reactive groups on the membrane.

The application of covalent coupling methods is obtainable with membrane systems which

contain reactive functional groups, i.e., hydroxyl (–OH), carboxyl (–COOH), and amine (–NH₂) groups. These reactive groups can be introduced on the membrane via the direct modification of the polymeric structure of the membrane or by the preparation of the membrane from suitable monomers which contain the desired functional groups.

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Biocatalytic Membrane Reactor

- ▶ [Biochemical Membrane Reactors](#)
- ▶ [Immersed Membrane Bioreactor \(IMBR\)](#)

Biocatalytic Membrane Reactor, Mass Transport in

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Synonyms

[Modeling of biocatalytic membrane reactor](#)

For creating a biocatalytic membrane layer, the biological catalyst such as whole cells (bacteria, yeast, mammalian and plant cells) is inoculated into the porous membrane layer where they are grown, or bioactive molecules such as enzymes are immobilized within the membrane matrix or in a thin layer on the membrane interface of the membrane layer. A medium is flowing through

the biocatalytic, mostly asymmetric, plain, or cylindrical (hollow fiber) layer, supplying the cells with oxygen and nutrients or the enzyme with reactant(s) while the wastes and desired products are removed (Drioli and Giorno 1999). The performance of a hollow fiber or sheet bioreactor is primarily determined by the momentum and mass transport rate (Bird et al. 1960) of the key nutrients through the biocatalytic membrane layer. Thus, the operating conditions (transmembrane pressure, feed velocity) and the physical properties of membrane (porosity, wall thickness, lumen radius, matrix structure, etc.) can considerably influence the performance of a bioreactor, the effectiveness of the reaction. The limited transport of nutrients can cause serious damage in production. The introduction of convective transport is crucial in overcoming diffusive mass transport limitation of nutrients especially of the sparingly soluble oxygen. The starting balance equations developed by Navier and Stokes (Bird et al. 1960; Seidel-Morgenstern 2010; Nagy 2011) can be essentially simplified, and the momentum and the mass transport expressions can often separately be solved in the case of biocatalytic processes. The principle of the mass transport of substrates/nutrients into the immobilized enzyme/cells, through a solid, porous layer (membrane, biofilm) or through a gel layer of enzyme/cells, is the same. The structure and the thickness of this mass transport layer can be very different; thus, the mass transport parameters, namely, diffusion coefficient, D ; convective velocity, v ; the bioreaction rate constant; their dependency on the concentration; and/or space coordinate are characteristics of the porous layer and the nature of the biocatalysts. Some assumptions made for expression of the differential mass balance equation to the biocatalytic membrane layer are as follows: reaction occurs at every position within the biocatalyst layer; mass transport through the biocatalyst layer occurs by diffusion and convection; mass transport parameters (diffusion coefficient, convective velocity, bioreaction rate constant) are constant; and the process is steady state. Thus, the mass balance equation can be given for a plain membrane layer as follows, applying, e.g., the

Biocatalytic Membrane Reactor, Mass Transport in, Table 1 Expressions of the important biocatalytic reactions

Substrate inhibition:	$Q = \frac{r_{\max} c}{K_{Mi} + c + c^2/K_c}$
Substrate inhibition and competitive product inhibition:	$Q = \frac{r_{\max} c}{K_{Mi} (1 + p/K_p) + c + c^2/K_c}$
Competitive product inhibition:	$Q = \frac{r_{\max} c}{K_{Mi} (1 + p/K_p) + c}$
Noncompetitive product inhibition:	$Q = \frac{r_{\max} c}{(K_{Mi} + c) (1 + p/K_p)}$

Michaelis-Menten (MM) kinetics (c denotes the concentration):

$$D \frac{d^2 c}{dy^2} - v \frac{dc}{dy} - \frac{v_{\max} c}{K_M + c} = 0 \quad (1)$$

The source term can be different in biocatalytic reactions; the most often applied equations are listed in Table 1. The inhibited reaction can take place in both the enzymatic and microbial reactions.

Two important cases can be discussed, namely, when the outlet (at $y = \delta$) diffusive flow is zero ($dc/dy = 0$, no sweep phase on the permeate side, case A) and $dc/dy \neq 0$ at $y = \delta$ (there is sweep phase on the permeate side, case B). The mass transfer rates are given by Eqs. 2 and 3 for cases A and B, respectively, for first-order reaction as limiting case of MM kinetics (Nagy 2011):

$$J = \left(\frac{D}{\delta} \right) \frac{\left(\frac{Pe^2}{4} + \Theta^2 \right) \tanh \Theta + Pe \Theta}{\left(\frac{Pe}{2} \tanh \Theta + \Theta \right)} c^0 \quad (2)$$

with

$$\Theta = \sqrt{\frac{Pe^2}{4} + \vartheta^2}, \vartheta = \sqrt{\frac{k_1 \delta^2}{D}}$$

$$J = \beta \left(c^0 - \frac{\Theta}{e^{Pe/2} [(Pe/2) \sinh \Theta + \Theta \cosh \Theta]} c_\delta \right) \quad (3)$$

with ($c = c_d$ at $y = d$ and $c = c^o$ at $y = 0$; $Pe = nd/D$)

$$\beta = \frac{D}{\delta} \frac{([Pe/2]\tanh\Theta + \Theta)}{\tanh\Theta}$$

The mass transfer rates are given by Eqs. 4 and 5 for cases A and B, respectively, for zero-order reaction as limiting case of MM kinetics (k_0 denotes the reaction rate constant):

$$J = \frac{D}{\delta} c^0 \left[Pe - \frac{\vartheta^2}{Pe} \left(1 - \frac{1}{e^{Pe}} \right) \right] \quad (4)$$

and

$$J = \frac{D}{\delta} \frac{Pe}{2} \times \frac{e^{Pe/2}}{\sinh(Pe/2)} (1 - T) \left[c^0 - \frac{e^{-Pe}}{1 - T} c_\delta \right] \quad (5)$$

with

$$T = \frac{\vartheta^2}{Pe^2} (e^{-Pe} [1 + Pe] - 1); \vartheta = \sqrt{\frac{k_0 \delta^2}{Dc^0}}$$

The flow through this membrane is proportional to the transmembrane pressure drop and inversely proportional to the fluid viscosity (Darcy law, Eq. 6) (κ is the permeability and μ is the fluid viscosity):

$$v_M = -\frac{\kappa}{\mu} \frac{dp_M}{dr} \quad (6)$$

Then, one can get from Eq. 6, for capillary membrane, as:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial (rv_M)}{\partial r} \right) \equiv -\frac{\kappa}{\mu} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial p_M}{\partial r} \right) = 0 \quad (7)$$

When Eq. 7 is integrated twice with respect to r with boundary conditions, at $r = r_o$ then $p_M = p_t$ and at $r = r_o + d$ then $p_M = p_e$, one gets the radial pressure and velocity distributions (Nagy 2011, pp. 178) within the membrane as:

$$p_M(r, z) = \frac{p_t(z) - p_e(z)}{\ln(1 + \delta/r_o)} \ln \frac{r}{r_o} + p_t(z) \quad (8)$$

$$v_M(r, z) = \frac{\kappa}{\varepsilon \mu} \frac{r_o}{r} \frac{p_t(z) - p_e(z)}{\ln(1 + \delta/r_o)} \quad (9)$$

The axial pressure distribution is given in entry “[Hollow Fiber Enzymatic Reactor, Modeling of.](#)”

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Biocatalytic Membrane Reactor, Modeling of

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There are two main types of membrane bioreactors: (i) the system that consists of a traditional stirred-tank reactor combined with membrane separation unit and (ii) the membrane that contains the immobilized biocatalysts such as enzymes, microorganisms, and antibodies and, thus, acts as a support and a separation unit. The biocatalyst can be immobilized in or on the membrane by entrapment, gelification, physical adsorption, ionic binding, covalent binding, or cross-linking (Giorno and Drioli 1999; Cabral et al. 2001). Modeling of stirred-tank reactor, for chemical reactions in it, is known (Westertep et al. 1993). This can easily be adapted for biochemical reactions applying the reaction kinetics given in entry “[► Biocatalytic Membrane Reactor, Mass Transport in.](#)” The momentum and

mass, energy transport through membrane as a separation unit, starting with Navier-Stokes equation (Bird et al. 1960), strongly depend on the separation process used (Baker 2004; Drioli et al. 2006; Nagy 2011). Immobilizing biocatalyst in the porous membrane matrix of an asymmetric membrane or onto membrane interface, the membrane layer can act as an active catalyst and a permselective layer. The biocatalytic membrane modules (plane and frame, hollow fiber capillary, tube as well as spiral membrane modules) can be divided into three sections: feed and permeate fluid phases and the biocatalytic membrane layer itself. Modeling of a membrane process means the simultaneous treatment of every section starting with Navier-Stokes equations for momentum, mass, and energy (Bird et al. 1960) adapting them to the real operating conditions and completing them by source or sink terms (Seidel-Morgenstern 2010). The energy balance equation is mostly negligible in case of biochemical reaction; the process can be regarded as isotherm; accordingly the continuity (conservation of mass), momentum, and component balance equations (see Eqs. 1–4 in entry “► [Hollow Fiber Enzymatic Reactor, Modeling of](#)”) should be simultaneously or consecutively (mass transport does not affect the velocities of fluids) solved after suitable simplification of a real system. The cylindrical effect should be taken into account for capillary membrane when the ratio of the membrane thickness and the internal radius is larger than about 0.05. The second-order pressure gradient can be expressed by Eq. (1) (Nagy 2011, p. 225). From that the radial and the axial velocity distribution in the feed (lumen) and the shell side can easily be obtained.

$$\frac{d^2 p_t}{dz^2} = \frac{8u_o \mu \zeta}{r_o^2 \lambda (1 + \zeta) \sinh(\lambda L)} \frac{1}{\lambda^2} \{ \cosh[\lambda(L - z)] - \langle 1 + f(1 + \zeta) \rangle \cosh(\lambda z) \} \quad (1)$$

with $[r_k]$ denotes the outer radius of hexagonal arrangement of the hollow fibers; f is the fraction of inlet feed directed out through the shell (Nagy 2011)]

$$\lambda = \sqrt{\frac{16\kappa}{r_o^3 \ln(1 + \delta/r_o)}} \left(1 + \frac{1}{\zeta} \right)$$

and

$$\zeta = \left(1 + \frac{\delta}{r_o} \right)^2 - \left(\frac{r_k}{r_o + \delta} \right)^2$$

The mass transfer rates for constant parameters are given in entry “► [Biocatalytic Membrane Reactor, Mass Transport in](#)” for limiting cases. An analytical approach is recommended by Nagy (2011) for the general Michaeli-Menten kinetics or bioreactions with two substrates feeding on the two sides of the membrane reactor. This method can take into account the effect of the in-space and/or time variable or concentration dependent parameters on the process.

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Biocatalytic Membrane Reactors

- [Membrane Bioreactors](#)
- [Principle of Biocatalytic Membrane Reactors \(BMR\)](#)

Biocatalytic Membrane Reactors (BMR) with Biocatalysts Entrapped Within the Pores of Asymmetric Membranes

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Synonyms

Catalytic membrane bioreactors with biocatalysts segregated within the pores of asymmetric membranes; Catalytic membrane reactors with biocatalysts segregated within the pores of asymmetric membranes

Polymeric and inorganic membranes with asymmetric structure have been used to segregate (by physical entrapment and adsorption) enzymes and microbial cells within the porous membrane structure (Drioli and Giorno 1999; Drioli et al. 1982).

Polymeric membranes have been cast with microbial cells in the casting solution using the phase inversion technique. A number of microorganisms can withstand high temperatures and organic solvents and have been entrapped in membranes. Microbial enzymes maintain their activity presumably because of cellular membrane protection. Cell-loaded membranes appear to be kinetically active and stable over a long period of time. It is noteworthy that cell entrapment can enhance microbial activity as compared to cell behavior in a homogeneous solution, an effect probably due to cellular membrane permeabilization as a consequence of the entrapment procedure.

Biocatalysts can also be entrapped in asymmetric membranes after their preparation, by cross-flow ultrafiltration, under operating conditions that promote fouling, where foulant molecules are the biocatalysts themselves. The retention of enzymes within the porous layer of the asymmetric membrane is very efficient when permeating

enzyme solution from porous to selective layer, where the pores in the selective layer are small enough to retain enzyme molecules but large enough to let products pass through.

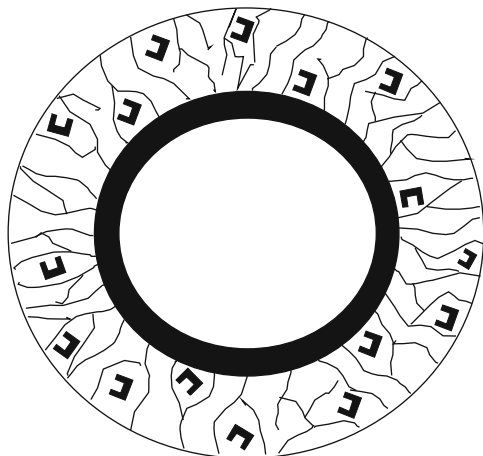
Enzymes are not able to work at high concentration; hence, the amount of immobilized catalyst strongly affects reactor performance. When the substrate is transported by convection through the enzyme-loaded membrane, the residence time is an important parameter to optimize.

For systems where the substrate is transported by diffusion, quick graphical procedures are available in literature for evaluating the extent to which external and internal diffusion affects immobilized enzyme kinetics (Engasser 1978; Bailey and Ollis 1986). Suggested models can be used to predict reactor performances in the case of enzymes with relatively simple kinetics (such as α -galactosidase, invertase, glucose isomerase, urease, fumarase) and when the kinetic and transport parameters are known.

The dynamics of substrate conversion depends on enzyme kinetics as well as on mass transport conditions.

Asymmetric hollow fibers with selective layer either on the lumen side or on the shell side can provide an interesting support for immobilizing enzymes. Figure 1 shows the case where the enzymes are effectively immobilized or segregated within the spongy annular section of an asymmetric hollow fiber containing the selective layer on the lumen side.

In this configuration, the substrate solution can be circulated along the shell side of the membrane module and permeated through the enzyme-loaded membrane under an applied transmembrane pressure as driving force. As the substrate permeates through the membrane containing the enzyme, it is converted to the reaction product. If the molecular weights of substrate and products are small, both can permeate through the membrane. This means that the permeate recovered from the lumen side of the membrane contains both reaction product and unconverted substrate. Measuring the reduced substrate concentration (or the increased product concentration) in the permeate during time operation, it



Biocatalytic Membrane Reactors (BMR) with Biocatalysts Entrapped Within the Pores of Asymmetric Membranes, Fig. 1 Cross-section of BMR with enzyme entrapped within the porous support

is possible to calculate the reaction rate and the conversion degree.

If the enzyme is immobilized only within the pores and not on the membrane surface, the concentration of the substrate in the retentate stream does not change, because only the solution that permeates through the membrane contacts the biocatalyst. The substrate is then continuously recycled to the tank and fed to the reactor at constant concentration (Giorno et al. 2001).

If the enzyme is also present on the membrane surface, some decrease of substrate concentration in the retentate stream is also observed. A blank experiment may confirm that when no enzyme is present on the membrane, no conversion occurs.

The conversion degree can be calculated as follows:

$$\text{Conversion} = \frac{C_r - C_p}{C_r} \quad (1)$$

where

C_r = concentration of substrate in the retentate solution

C_p = concentration of substrate in the permeate solution

This gives the conversion at each passage through the membrane pores that basically work as high-throughput microreactors.

When the enzyme is also immobilized on the membrane surface, it is necessary to take into account the conversion of the substrate in the retentate solution, and then the total conversion is calculated as:

$$\text{Total conversion} = \frac{(C_r - C_p) + (C_i - C_r)}{C_i} \quad (2)$$

where C_i is the initial substrate concentration.

The reactor volume is represented by the void volume of the porous asymmetric membrane. Under convective flow, each macrovoid of the asymmetric membrane can work in conditions of continuous stirred tank reactor. If this assumption is applicable, the reaction rate equation can be derived by the balance equation at steady state:

$$QC_f - QC_p + v_r \cdot V = 0 \quad (3)$$

Resolving for v_r , the following is obtained:

$$v_r = \frac{Q(C_f - C_p)}{V}$$

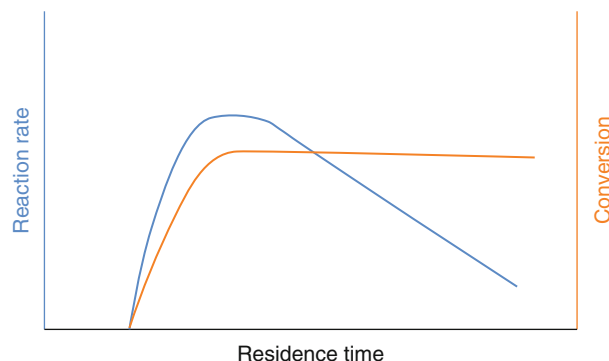
where v_r is the reaction rate ($\text{mmol} \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$); Q is the filtration flow rate ($\text{cm}^3 \cdot \text{min}^{-1}$); C_f and C_p are the feed and permeate concentration ($\text{mmol} \cdot \text{cm}^{-3}$), respectively; and V is the reactor volume (cm^3).

The general behavior of reaction rate and conversion as a function of residence time assumes the form qualitatively illustrated in Fig. 2.

Increasing the residence time means decreasing of the filtration flow rate (Q); therefore, reaction rate increases as long as higher residence time means more interaction between the substrate and the immobilized enzyme. After the residence time to saturate enzyme is reached, C_f and C_p in Eq. 3 are constant, and further increase of residence time (i.e., decrease of filtration flow rate) causes a decrease of the reaction rate (Mazzei et al. 2012).

Biocatalytic Membrane Reactors (BMR) with Biocatalysts Entrapped Within the Pores of Asymmetric Membranes,

Fig. 2 Behavior of reaction rate and conversion as a function of residence time in a continuous stirred tank membrane reactor



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Biocatalytic Membrane Reactors with Chemically Bound Enzyme

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Synonyms

Biocatalytic membrane reactors with covalent bound enzyme; Immobilized enzyme

Attachments of biocatalysts to membrane can result from ionic binding, cross-linking, and covalent linking. Since 1954, when protease was covalently bound to diazotized polystyrene, enzyme immobilization via covalent bonds has been an established immobilization technique, usually carried out by means of bi/multifunctional reagents, such as glutaraldehyde, (3-aminopropyl) triethoxysilane (APTES), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), etc.

The crucial aspect is the use of mild reaction conditions that do not denature the enzyme during the covalent bond formation.

When the extent of initial denaturation is acceptable in the economics of the process, enzymes bound to membranes can be used in continuous flow reactors.

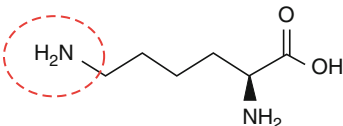
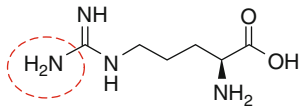
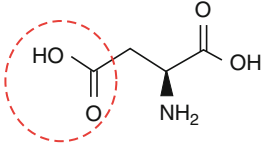
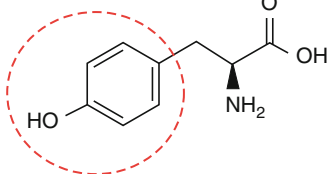
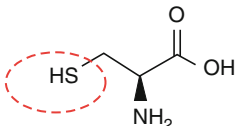
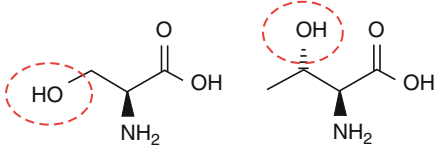
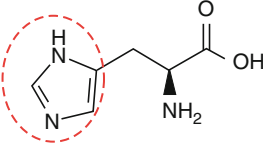
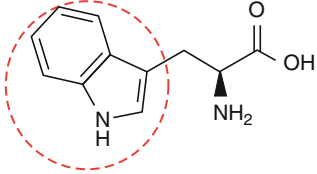
Table 1 shows the protein functional groups involved in covalent bond with functional groups present or grafted on the membrane, in mild conditions.

Table 2 summarizes most commonly used cross-linking agents to bridge enzyme to functionalized membranes.

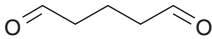
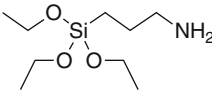
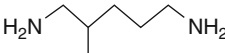
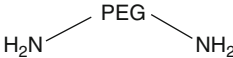
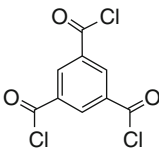
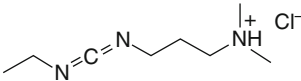
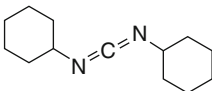
Hydrophilic, hydrophobic polymeric membranes as well as inorganic membranes can be used as support for covalent bound of enzymes.

Polymeric membranes based on natural materials, such as cellulose and its derivatives (regenerated cellulose, cellulose acetate, etc.) have been extensively used as support for the covalent immobilization of enzymes. Cellulose membranes can be activated by a variety of agents

Biocatalytic Membrane Reactors with Chemically Bound Enzyme, Table 1 Protein functional groups involved in covalent bond with membranes in mild conditions

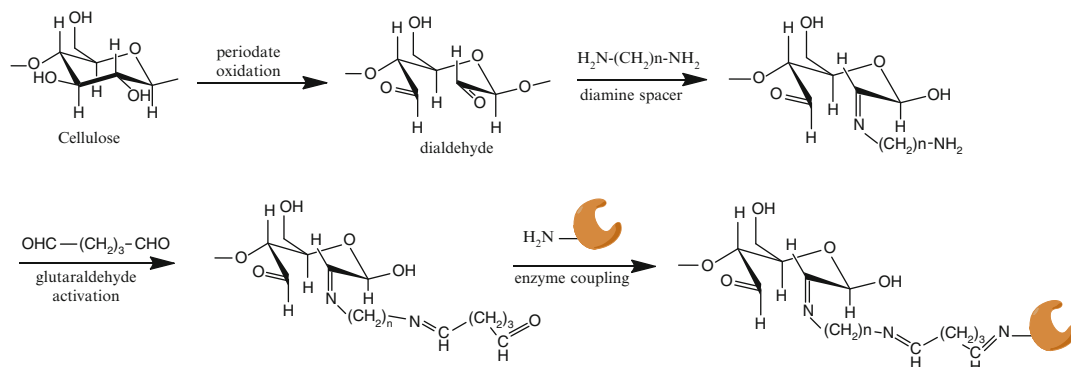
Protein chemical group	Structure
Epsilon amino groups of lysine	 The structure shows the side chain of lysine: a four-carbon chain starting from the alpha-carbon (which is bonded to an amino group and a carboxylic acid group). The terminal carbon of this chain has an amino group (H ₂ N), which is circled in red.
Epsilon amino groups of arginine	 The structure shows the side chain of arginine: a three-carbon chain starting from the alpha-carbon (bonded to an amino group and a carboxylic acid group). The terminal carbon is part of a guanidinium group (C(=NH)NH ₂), where the terminal amino group (H ₂ N) is circled in red.
Beta and gamma carboxyl groups of aspartic and glutamic acids	 The structure shows the side chain of aspartic acid: a two-carbon chain starting from the alpha-carbon (bonded to an amino group and a carboxylic acid group). The terminal carbon has a carboxylic acid group (HO-C=O), which is circled in red.
Phenol ring of tyrosine	 The structure shows the side chain of tyrosine: a three-carbon chain starting from the alpha-carbon (bonded to an amino group and a carboxylic acid group). The terminal carbon is part of a phenol ring (benzene ring with an OH group), which is circled in red.
Thiol group of cysteine	 The structure shows the side chain of cysteine: a two-carbon chain starting from the alpha-carbon (bonded to an amino group and a carboxylic acid group). The terminal carbon has a thiol group (HS-), which is circled in red.
Hydroxyl groups of serine and threonine	 Two structures are shown. On the left is serine, with a one-carbon side chain ending in a hydroxyl group (HO-), circled in red. On the right is threonine, with a one-carbon side chain ending in a hydroxyl group (OH), circled in red.
Imidazole group of histidine	 The structure shows the side chain of histidine: a two-carbon chain starting from the alpha-carbon (bonded to an amino group and a carboxylic acid group). The terminal carbon is part of an imidazole ring, which is circled in red.
Indole group of tryptophan	 The structure shows the side chain of tryptophan: a three-carbon chain starting from the alpha-carbon (bonded to an amino group and a carboxylic acid group). The terminal carbon is part of an indole ring system, which is circled in red.

Biocatalytic Membrane Reactors with Chemically Bound Enzyme, Table 2 Bi/multifunctional reagents commonly used in enzymatic covalent immobilization

Cross-linker	Structure	Reactive chemical group
Glutaraldehyde (GA)		Aldehydic groups
(3-aminopropyl) triethoxysilane (APTES)		Ethoxyl and amino groups
Dimethylaminopropane (DAMP)		Amino groups
O, O'- Bis(2-aminopropyl)-polyethylene glycol 500 (bNH2PEG)		Amino groups
1,3,5-benzene tricarbonyl chloride (or trimesoyl chloride TMC)		Carbonyl chloride groups
1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) <i>Spacer Arm 0.0 Å</i>		Carbodiimide group
Dicyclohexylcarbodiimide (DCC) <i>Spacer Arm 0.0 Å</i>		Carbodiimide group

to produce reactive centers for the covalent binding of enzymes. Its chemical structure is mainly composed of hydroxyl groups, and then the most common activation methods are based on the conversion of the hydroxyl groups into more reactive functional groups. In particular, carbonyl groups are very suitable for enzyme immobilization since they can react with primary amines from enzymes (ϵ -amino group of lysine residues) to form imine. The most used method of forming carbonyl groups onto the cellulose skeleton is periodate oxidation. The hydroxyl groups (secondary alcohol groups) of the glucose units are oxidized into

the corresponding aldehydes by means of sodium periodate (NaIO_4). The covalent binding of the enzyme can be achieved by direct reaction with the aldehyde-active groups on the membrane surface (Xiao-Jun et al. 2011) or via different spacers. The introduction of an appropriate spacer between the enzyme and the membrane often improves the performance of immobilized enzyme, such as enzyme stability and retained activity. Spacers of different lengths are generally introduced by using bifunctional agents such as diamines (esp. ethylenediamine, pentaethylenhexamine, etc.) that are coupled or activated with glutaraldehyde



Biocatalytic Membrane Reactors with Chemically Bound Enzyme, Fig. 1 Schematic representation of an enzyme covalently immobilized onto cellulose membrane

activated with periodate oxidation and a generic diamine spacer, n represent the number of CH_2 groups

before enzyme immobilization (Peng-Cheng et al. 2011). The reaction mechanism involves the amino groups of the enzyme and the aldehyde groups of glutaraldehyde on the membrane surface. The schematic representation of an enzyme covalently attached onto cellulose-activated membrane is reported in Fig. 1.

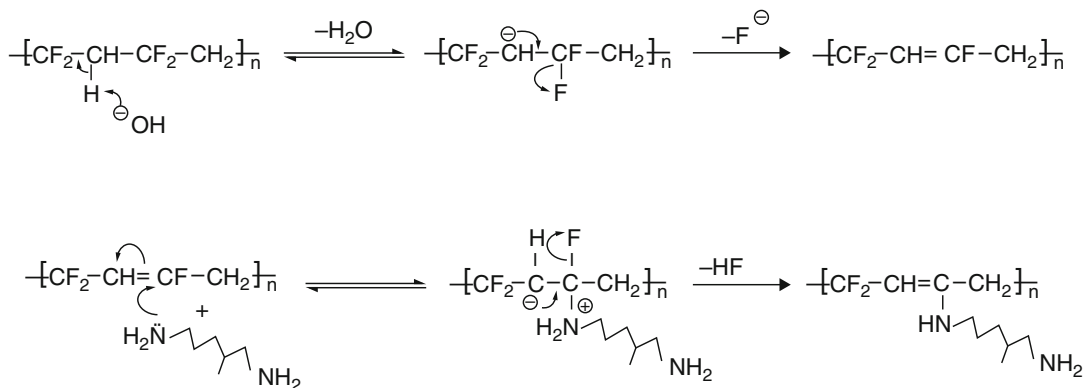
Poly(vinylidene fluoride) (PVDF) membrane has been used either for scientific research or industrial application in particular micro- and ultrafiltration process. The great interest to PVDF membrane is due to its extraordinary thermal, mechanical, and chemical resistance in addition to membrane-forming properties. Its structure consisting of repeated $-(\text{CH}_2-\text{CF}_2)_n-$ units confers to PVDF these good properties, but makes impossible enzyme immobilization on native PVDF in a covalent manner. This disadvantage can be overcome performing PVDF functionalization, in order to introduce on the polymeric membrane structure, reactive groups that can covalently couple with enzyme functional groups. Surface modification of existing PVDF membrane can be performed by coating or grafting. Coating modification is preferred when only an improved hydrophilicity of the membrane surface is required, but it is not useful as anchor point for enzyme immobilization because of the instability of the coated layer which interacts with the membrane merely by physical adsorption. More

interesting for enzyme immobilization is grafting modification which can introduce on the PVDF backbone functional chains that can be used for enzyme immobilization; in addition acting on degree of grafting and type of functional chain introduced, it is possible to affect or not affect membrane bulk properties as, for example, hydrophobicity.

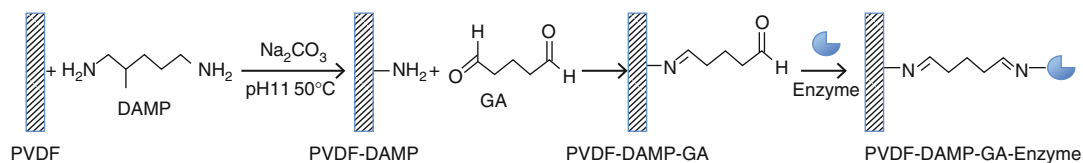
Surface grafting can be performed by high-energy radiation techniques like plasma treatment, ozonation, and UV or by wet chemistry in harsh basic environment. For example, grafting of amino groups on PVDF membrane surface can be achieved by treatment at high pH and high temperature with diamine reagent. The high pH promotes fluorine elimination from the PVDF chains and the grafting of diamino reagent (Vitola et al. 2015) (Fig. 2).

Subsequently the pendant amino groups can be activated for enzyme immobilization in mild conditions using condensing reagent like glutaraldehyde (Fig. 3).

Polymeric membrane based on polyethersulfone (PES) is widely used membranes in ultrafiltration processes due to their high performance and low-cost profile. PES membranes have been used also in more sophisticated application such as carrier for immobilization of bioactive molecules in membrane bioreactors. For this aim effort has been done to introduce reactive



Biocatalytic Membrane Reactors with Chemically Bound Enzyme, Fig. 2 Possible mechanism of alkaline-induced DAMP grafting on PVDF



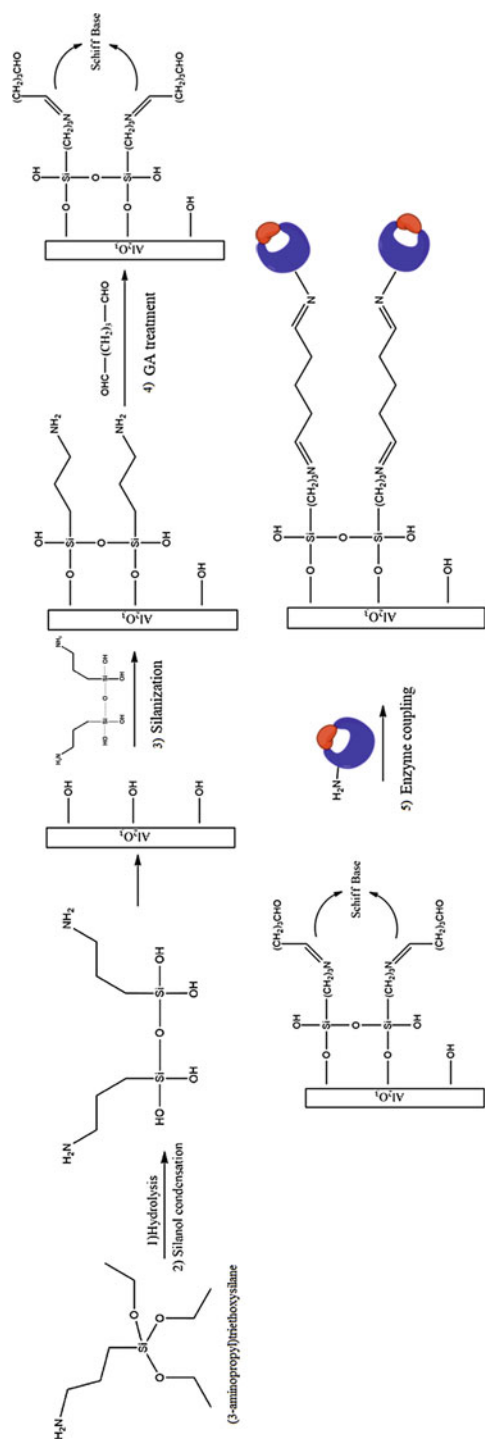
Biocatalytic Membrane Reactors with Chemically Bound Enzyme, Fig. 3 Illustration of various steps for PVDF functionalization with amino groups and subsequent enzyme attachment via cross-linking with glutaraldehyde

groups for biomolecule immobilization without affecting the overall bulk properties. Photochemical surface modification of existing PES membrane is the most popular technique for introduction of reactive groups on PES membrane. In fact PES has an intrinsic photoreactivity making possible to perform the modification in mild reaction condition. Monomer like acrylic acid has been grafted in this way on PES membrane and then activated for enzyme immobilization using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC).

Inorganic membranes, such as alumina, titania, silica, etc., can be also used for enzymatic immobilization via covalent binding if functionalized in a suitable way. Hydroxyl groups present onto inorganic membrane surface are not able to directly coupling enzymes. Activation of hydroxyl groups can be performed by silanization reagents, such as (3-aminopropyl)triethoxysilane (APTES).

APTES exhibits terminal amino groups available for the attachment of cross-linking reagents such as glutaraldehyde. Terminal aldehydic group of glutaraldehyde reacts with the exposed amino groups of the organosilane by forming a Schiff base. Final covalent binding occurs through formation of a new Schiff base between aldehydic terminal group of glutaraldehyde and amino groups exposed from the enzymatic amino acid residues of lysine (S. Tanvir et al. 2009). Schematic reaction of an example of enzymatic covalent immobilization onto inorganic supports is illustrated in Fig. 4.

Applications of covalently immobilized membrane systems are membrane electrodes for analytical purposes, reactions of substrates whose molecular weight is low as compared to membrane molecular weight cut-off, and enzymatic conversion of macromolecules to lower molecular weight species able to permeate the supporting membrane.



Biocatalytic Membrane Reactors with Chemically Bound Enzyme, Fig. 4 Schematic representation of stages involved in an example of enzymatic covalent immobilization onto inorganic membranes

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Biocatalytic Membrane Reactors with Covalent Bound Enzyme

► Biocatalytic Membrane Reactors with Chemically Bound Enzyme

Biocatalytic Membrane Reactors with Site-Specific Immobilized Enzyme

Yamini Satyawali¹, Ehiازه Augustine Ehimen² and Winnie Dejonghe²

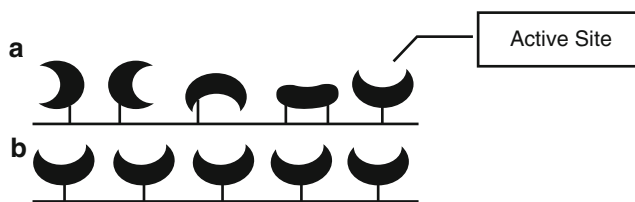
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Membranes are used in bioreactors as selective barriers and sometimes also as a support/carrier matrix for enzyme immobilization. Such reactors are referred to as biocatalytic membrane reactors (BMRs). The immobilization of enzymes on membranes can be of two types: (i) nonspecific immobilization or (ii) specific immobilization (Fig. 1). Nonspecific immobilization is often random and proceeds through the numerous lysine residues on

the protein. In this process, enzymatic activity is significantly decreased largely due to different orientations of the enzymes with respect to the membrane or to multiple point attachment which also renders the active site inaccessible for the substrates or sometimes results in complete denaturation of enzymes. Methods of nonspecific immobilization include adsorption, nonspecific covalent binding, entrapment, and encapsulation. Therefore, it is essential to develop methodologies for site-specific immobilization of the enzymes with the active (or binding) site directed away from the membrane. This would ensure that benefits of enzyme immobilization could be availed without compromising on their activity.

Specific immobilization or site-specific immobilization of enzymes depends a lot on the type of enzyme and support material (membranes in the case of biocatalytic membrane reactor). Depending upon the enzyme structure and characteristics, various strategies can be used to conduct site-specific immobilization (Butterfield et al. 2001). For example, if an enzyme does not contain any cysteines (or any cysteines that are required for activity), then the site-directed mutagenesis approach may be used. This approach aims at introduction of unique cysteines to enzymes. The enzymes are attached on thiol-reactive surfaces through the sulphydryl group on the side chain of the introduced cysteine, which is located on the opposite side of the protein from the active site. An example of such an enzyme is subtilisin, a protein normally devoid of cysteine (Vishwanath et al. 1998). Another approach in this field is gene fusion which is used to incorporate a peptidic affinity tag at the N- or C-terminus of the enzyme. The enzymes are then attached from this affinity tag to anti-tag antibodies on membranes. The gene fusion approach is appropriate when the N- or C-terminus of the enzyme are away from the active site. Gene fusion methods have been employed to investigate site-specifically immobilized alkaline phosphatase (AP) on functionalized membranes (Vishwanath et al. 1997). Another method considered to be of biomimetic inspiration is the posttranslational modification to incorporate a single biotin moiety on enzymes. The enzymes can be attached to membranes through a (strept)-avidin bridge.



B

Biocatalytic Membrane Reactors with Site-Specific Immobilized Enzyme, Fig. 1 (a) Random immobilization of enzymes, showing potential difficulties. (b) Site-specific immobilization of enzymes to form an

array of similarly oriented proteins, always with the active site away from the polymer surface (Butterfield et al. 2001)

This modification incorporates a biotin moiety on a specific lysine residue on the enzyme, which allows the use of an avidin spacer between the enzyme and the immobilization surface. Biotin, a vitamin, has an affinity for avidin, a protein found in egg whites, that is a remarkably strong association. An example of such an enzyme is beta galactosidase immobilization on polyethersulfone membranes (Vishwanath et al. 1995).

From the membrane point of view, some of the approaches for site-specific attachment of the enzyme include modifying the membranes by attaching functional groups such as sugar and polypeptides to which the enzymes eventually bind (Mazzei et al. 2010).

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Biochemical Conversion

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Biochemical conversion refers to the application of biologically mediated processes to facilitate the production of a range of chemical products and power. This conversion route involves the direct use of living organisms (i.e., whole cells) or desired active protein constituents (i.e., enzymes and antibodies) extracted from living cells to aid the reformation of reactant species to desired products or the synthesis of new chemicals.

Biochemical conversion processes thus rely on biocatalytic transformation systems for achieving synthetic chemistry goals. Historically, such processes have been applied for centuries for alcohol (via fermentation) and cheese (via enzymatic degradation of milk proteins) production in different geographical regions globally using different techniques but with similar underlying conversion principles. Increased knowledge on protein structure (including protein design tools, i.e., rational design and directed evolution) and function relationships has further improved scientific understanding of biochemical conversion processes and thus has helped to advance its adaptation, implementation, and application (up to industrial scales) in recent decades.

The substrates employed for biochemical conversion schemes can be derived directly or

indirectly from biomass sources (i.e., plant and animal) as in the case of the anaerobic digestion of biomass for the production of a range of volatile fatty acids (carboxylic acids with chain lengths C_1 – C_5) and methane (CH_4) which have applications in the chemical and energy industry, respectively. Here, a multistage degradation of the complex polymers and compounds (which make up the biomass substrate) to lower molecular weight products is facilitated by a consortium of anaerobic bacteria (whole cells). The enzymatic transesterification or esterification of biologically obtained triglycerides to fatty acid methyl esters using the enzymes-lipases is another example of such bio-derived substrate for biochemical conversion. The conversion of non-biomass-derived substrates is also feasible, with the synthesis of new chemical products, obtainable via the transformation and degradation of chemical reactants with the application of biochemical conversion methods. An example is the asymmetric synthesis of chiral amines from prochiral ketones (which has a significant interest from pharmaceutical industries), i.e., 4-phenyl-2-butylamine production via the transamination of 2-propylamine and 4-phenyl-2-butanone with ω -transaminases used as the process biocatalyst. With approximately 100 different biocatalyst-mediated processes applied in the pharmaceutical, food, chemical, agricultural, and cosmetic industries, the product ranges from biochemical conversion processes range from specialist research and commodity chemicals, to food and fuel products (Wandrey et al. 2000).

With the biochemical conversion schemes highly dependent on the use of biocatalytic processes for achieving product synthesis, the major advantage with the use of this route is the high selectivity obtainable. This selectivity which can be chiral (i.e., stereoselectivity), positional (i.e., region selectivity), and functional group specific (i.e., chemo-selectivity) is highly desirable in chemical synthesis since it may offer benefits such as the none or reduced use of protecting groups, a minimization of side reactions, ease in downstream separation of products, and possible

fewer environmental issues (Johannes et al. 2006). Compared with chemical and thermochemical conversion technologies, the application of biochemical conversion processes has been highlighted to be generally more efficient (with a lower biocatalyst concentration employed compared to chemical catalysis requirements) with milder process reaction conditions (usually with temperature and pH ranges of 20–40 °C and 5–8, respectively, for most biochemical processes) as opposed to the harsher pressure, temperature, and pH operation conditions usually applied for chemical conversions. Biochemical conversion technologies also possess the advantage of being modifiable to increase selectivity, stability, and activity of the applied biocatalyst to improve the product yields of the targeted conversion process, the possibility of the biocatalyst recycling (which could aid a reduction in the process wastes and costs), and potentially having superior environmental benefits (i.e., nontoxic by-products or side reactions, non-production of process effluents, and reduced energy process inputs) compared with the use of chemical/thermochemical conversion schemes.

The main disadvantages with the use of biochemical conversion systems are its inhibition susceptibility (including substrate and product inhibition), the limiting operation ranges where biochemical conversions can be applied (since biocatalysts usually have an optimal operational pH, temperature, etc.), and the water requirements for most processes (which could potentially be disadvantageous from a downstream processing and energetics perspective).

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Biochemical Membrane Reactors

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Synonyms

Biocatalytic membrane reactor

A biocatalytic membrane reactor (also referred to as a biochemical membrane reactor) is a system or device that combines and utilizes the separation capabilities of membranes and the catalytic activities of whole cell or enzyme biocatalysts in one unit to facilitate the biochemical conversion of substrates into desired products and the selective removal of the products in a single process unit. The removal of the product components from the reaction site could in turn improve the conversion of the substrates by favoring the product formation reaction and is thus useful for reactions that are thermodynamically unfavorable or are product inhibited. The separation of permeable solutes can be achieved from the reaction mixture by the action of a driving force that is applied across the membrane. As a result of coupling the conversion reaction with separation, lower operating costs could therefore be achievable with this type of reactor design compared to the use of multiple reaction and product separation methods.

The complete retention of the biocatalyst within the reactor system is the most important requirement for the successful continuous operation of biocatalytic membrane reactors. Ultrafiltration membranes with a pore size distribution range (nominal molecular weight cutoff, NMWCO, of 500–100 kDa) are the most adequate for the retention of a majority of native or

modified enzymes (10–100 kDa) (Prazeres and Cabral 1994).

The biocatalyst is usually present in the reactor system in two forms: free or immobilized at the membrane surface, or inside the membrane matrix pores. If the biocatalyst (i.e., enzyme) is present in its free form, its immobilization can be achieved by confining the enzyme to one side of the membrane unit. This can be facilitated by size exclusion, electrostatic repulsion, or enlargement via chemical or physical immobilization techniques onto an intermediate support (i.e., inert proteins and gels). As for the direct immobilization of the biocatalyst onto the membrane, this can be achieved by chemical binding, physical adsorption, or electrostatic attraction.

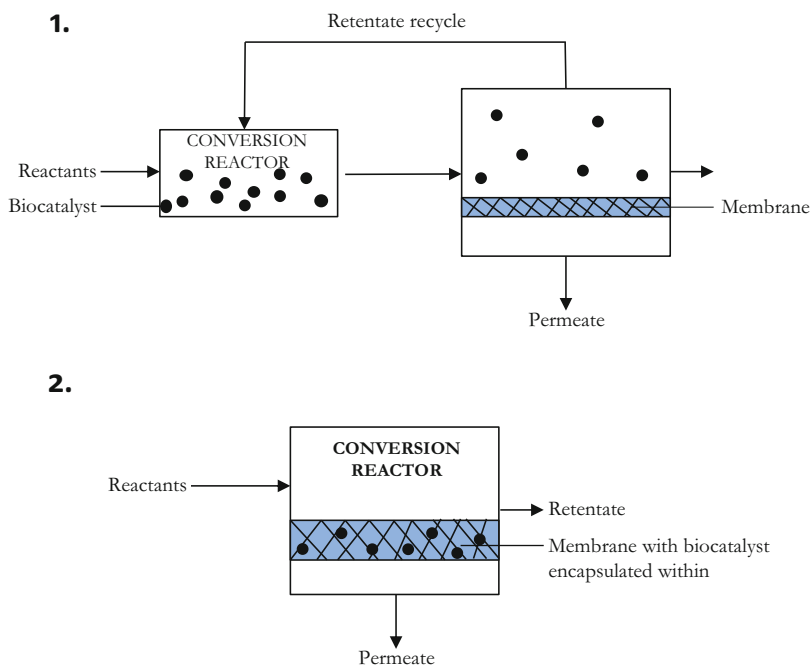
Ideally, the products resulting from the biocatalytic process should permeate through the membrane pores either via a concentration gradient-induced diffusion or a pressure gradient-induced convection. This would in turn facilitate a continuous removal of products from the reaction media, a process which has been considered to be essential for biocatalytic membrane reactor concepts. The selection of the membrane unit to be incorporated into the reactor system must take into account the respective sizes of the enzymes, substrates, and products, as well as the chemical characteristics of the reacting species and of the membrane. Here, the solute rejection coefficient is an important membrane selection parameter for the reactors and should be zero and one for the products and the biocatalysts, respectively (Prazeres and Cabral 1994). This would allow for the product/coproduct permeation through the membrane and a complete retention of the biocatalysts inside the reaction system.

The configurations of biocatalytic membrane reactors can be categorized into two main types (Fig. 1) (Giorno and Drioli 2000):

1. The biocatalyst (i.e., whole cells, enzymes, or antibodies) are used in solution for the conversion of the substrate to the desired products in a reactor and further transported to a reaction vessel containing a selected membrane where

Biochemical Membrane Reactors, Fig. 1

Main configuration types for biocatalytic membrane reactors; (1) conversion reactor combined with a membrane unit, (2) submerged membrane reactor with the membrane functioning as a catalytic and separation unit (Adapted from Giorno and Drioli 2000)



Biochemical Membrane Reactors, Table 1 Advantages and disadvantages of biocatalytic membrane reactors (Prazeres and Cabral 1994)

Advantages	Disadvantages
Possibility of developing continuous conversion processes	Unfavorable adsorption and enzyme-poisoning issues
Improved control of reaction systems	Enzyme deactivation due to shear-related effects
Increased productivities	Concentration polarization
Contribute in a favorable shift of the reaction toward product side	Likely product/substrate inhibition at the membrane surface
Better conversion rates in product-inhibited reactions	Membrane fouling
Good product enrichment and concentration in process stream	Enzyme leakage
Facilitates control of the molecular weight of hydroxylates	
Allows the conducting of multiphase reactions without emulsification issues	
Useful refined research tool for studying enzyme mechanisms	

the biocatalysts (and unreacted substrates) can be recycled back to the conversion reactor, with the permeate selectively extracted from the reaction stream. Here, the biocatalytic membrane reactor system might consist of a conventional stirred-tank reactor combined with a membrane separation unit.

2. The biocatalyst constituents are immobilized within the membrane of the matrix. Here, the

membrane acts as a support system for the biocatalyst as well as a separation unit.

The membrane units of the membrane reactor system can comprise of membranes which have a flat sheet shape (i.e., arranged in a plate and frame module or a spiral wound module) or tubular (assembled in a tube – and – shell module) (Giorno and Drioli 2000) (Table 1).

Cross-References

- [Biocatalytic and Biochemical Membrane Reactor](#)
- [Membrane Bioreactors](#)
- [Principle of Biocatalytic Membrane Reactors \(BMR\)](#)

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Biochemical Processing

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Biochemical processing refers to the use of biologically derived or biochemical techniques to meet the following goals: (i) to facilitate the conversion of specific substrates to products, (ii) as a process pretreatment scheme for the production of intermediates with the aim of achieving increased production yields or quicker conversion times, and (iii) to aid the recovery, recycling, or purification of a process intermediate or product.

Particularly in biochemical processes such as fermentation, the need for purification and concentration of the components is highly significant. Cell removal, whole broth clarification, downstream recovery, and purification of bioproducts from invariably dilute and often complex aqueous mixtures form an important aspect of biochemical processing. Furthermore, up to a few years, the

major amount of pharmaceuticals was produced via chemical synthesis processes. Nowadays, biotechnology productions dominate the pharmaceutical market, and membrane technology operations come to the fore due to the requirements of higher productivities.

In fact, membrane processes have been used in biochemical processing since well before the start of the modern membrane industry. Membrane technology for enzyme concentration, analysis of bacteriophages and viruses, preparation of cell- and protein-free ultrafiltrates from biological solutions, and sterile filtration has been widely used. These systems were however limited to analytical-scale processes due to limitations on the available membranes and modules. Over the last two decades, new membranes, modules, and systems have been developed specifically to meet the requirements of the biotechnology industry (Reis and Zdney 2007).

Particularly, in biochemical processes, with the technological advancements such as increased product titers of cell cultures from 1 to 3 g/L up to concentrations of 10 g/L, membrane unit operations found a stronger application throughout the production, purification, and formulation of biotechnology products. The membrane processes are applied in upstream applications including sterile filtration of fermentation media, pH control solutions, and gases. Furthermore, microfiltration may be used for turbid streams, virus filtration to protect cell cultures from introduction of viral contaminants in media, and ultrafiltration to remove, e.g., glycine, hypoxanthine, and thymidine from serum. On the other hand, in downstream processing, multiple operations are used such as sterile filtration of buffers, products and gases, and further membranes are integrated as sieving filtrations or as membrane chromatography steps. Ultrafiltration is used to concentrate and buffer exchange (diafiltration) products throughout the downstream process and is also used as the method of choice for final formulation of bulk product. Membrane chromatography can be used for purification of products and raw materials, e.g., the removal of endotoxins from raw materials, before using them in downstream processing. Membrane technology has high

potential in the field of biopharmaceutical production, and this needs to be fully exploited in the coming years (Fröhlich et al. 2012).

In addition, bioconversion processes such as production of biofuels from biomass (biorefinery concept) are also a suitable example of biochemical processing. Typical technologies that have been incorporated into the process include ion exchange resins that are being used for the detoxification of fermentation hydrolyzates, distillation in the recovery of ethanol and ethanol dehydration, and membrane separation for the removal of water from ethanol solution (Huang et al. 2008).

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Biochemical Recovery

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An important step in any biochemical processing or conversion is the recovery of the process intermediates or products of interest. This is especially important since most biochemical processes are conducted using very dilute conditions, with the desired product concentration as required which in turn varies over a wide range. The final product concentration and thus the extent of the product recovery is highly dependent on the preceding process/reaction conditions and the market costs

of the biochemical products. For example, for some organic acid fermentations, i.e., citric acid and glutamic acid, concentrations of 100 g/L or greater can be achieved (Wang 1983). Alternatively, with some more complex, specialized macromolecular products, i.e., vitamin B₁₂ and human insulin, concentrations of 1 g/L or less are usually considered to be satisfactory since these products command premium prices (Wang 1983). Applying schemes for concentrating the product in the medium from which it must be recovered is thus required and usually constitutes a significant cost. Depending on the medium/reaction dilution levels and the type of product recovery route applied, the recovery costs and in turn total process costs could be quite high. The extent of product concentration and purification achieved by the applied recovery process has a direct implication on the product costs and the profitability of the process, with an almost linear relationship demonstrated between the selling price of biochemical products and the concentrations of the products (Belfort 1989).

The product purification and its concentration are thus the two main considerations and form the basis guiding the selection of suitable downstream recovery schemes for biochemical processes. Ideal recovery systems should therefore strive for the reduction of the volumes of the medium, and a purification of the desired products while concentrating.

For the recovery of products from the dilute reaction medium, in addition to the extent of the dilution of the desired product, the medium constitution and complexity is also a factor which must be considered. This is because different classes of materials are usually present in the biochemical process streams (i.e., suspended and colloidal solids, microorganisms and cell debris, macromolecular solutes and microsolute) (Michaels and Matson 1985). The different size ranges exhibited by these medium components therefore pose a significant separation issue which must be carefully considered before a recovery scheme is applied. Furthermore, the fact that some biochemical products are normally susceptible to degradation due to changes in the temperature, ionic strength, pH, shear rate, and solvent conditions adds to the need for careful planning of the product recovery route (Michaels and Matson 1985).

Biochemical Recovery, Table 1 Conventional and membrane bioseparation technologies for product recovery (Michaels and Matson 1985)

Unit operation	Conventional process or equipment	Membrane process applicable
Cell harvesting	Rotary vacuum drum	Crossflow microfiltration (MF)
	Filtration	Ultrafiltration (UF)
	Centrifugation	
Whole broth clarification	Centrifugation	Crossflow MF, UF
Protein concentration/purification	Electrolyte/solvent precipitation	UF
	Affinity column chromatography	Diafiltration
		Membrane modulated protein precipitation
		UF affinity purification
		Membrane-bound affinity ligand chromatography
Desalting	Size-exclusion chromatography	Electrodialysis
Microsolute concentration	Vacuum evaporation	Reverse osmosis
		Pervaporation
		Membrane distillation
Acid/base recovery	Chemical treatment	Bipolar electrodialysis
	Ion exchange	
Solvent extraction	Podbielniak extraction	Membrane contactor solvent extraction

Different approaches can be applied to achieve an optimized recovery of the biochemical products, and there is no universal optimized recovery route applicable to every process; instead, the recovery options are usually selected to particularly suit the individual process and product case under consideration. The selected recovery process is also quite important especially since the recovery costs for some products have been reported to be considerably greater than the bioprocessing costs for the production of the product.

The selection of a suitable, industrial scalable recovery process is an important step in the downstream processing of products. The use of recovery methods such as adsorption, centrifugation, electrophoresis, chromatographic, solvent extraction, and membrane processes has been largely applied for biochemical processes. The different available recovery technologies can be selected on the basis of the manipulation of specific molecular characteristics of the desired product such as its molecular size, diffusivity, ionic charge, vapor temperature and pressure, solubility, surface activity, and its density.

The application of membrane techniques and its use for biochemical product recovery will be the main emphasis of this section.

Table 1 provides a summary of common biochemical product recovery unit operations and examples of conventional separation techniques usually applied for the desired product recovery. A comparison with the membrane processes which can also be applied for such processes are also presented in Table 1.

The selected biochemical recovery scheme, especially with the use of membrane techniques, can either be carried out as a downstream process (where the biochemical process is run batchwise) or integrated with the biochemical reaction, i.e., the use of in situ product recovery (or coproduct) methods. With the latter, the biochemical processing can be conducted continuously with the process reactants, and biocatalysts returned back or retained in the reactor. The use of such a method, in addition to the concentration and recovery of the desired product, might also help improve the biochemical process to favor the product formation (i.e., since its continuous removal will favor a shift of the reaction equilibrium toward product production).

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Biocidal and Self-Polishing Surfaces

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Biocidal and self-polishing surface is a surface that features the capability of preventing the settlement and colonization of biofouling microorganisms through biocide release and surface smoothing via a gradual hydrolysis of the paint film in wet environments. Biofouling is defined as the undesirable adhesion, adsorption, accumulation of microorganisms, plants, animals, proteins, and cells, etc., on a wetted surface, and it is of high concern in shipping industry. Biofouling on vessels increases hull roughness and hydrodynamic drag, which leads to a decrease in vessel performance and an increase in fuel consumption (Kirschner and Brennan 2012). Furthermore, hull maintenance of extensively fouled ships is costly as it is difficult to remove the biofilm. It is estimated that the fuel consumption can increase more than 40 % for a heavily fouled ship. Governments and industries around the world spend more than US\$ 5.7 billion annually to prevent and control marine biofouling (Yebra et al. 2004). A biocidal surface is usually designed by impregnation of coating with biocides which are released to kill the near microbes and resist biofouling. However, the release of heavy metal-based biocides from antifouling paint films often leads to an adverse impact on the marine environment and

more specifically on nontargeted marine livings due to their high persistence and toxicity. In recent years, some biocidal surfaces containing antimicrobial groups have been designed to kill and/or release the contacted microbes without leaching out biocides. These nontoxic biocidal surfaces have been developed and used in ship antifouling to meet the restrictive legislations (Siedenbiedel and Tiller 2012).

A self-polishing surface means the surface is able to keep smooth and clean through continuous polishing from the hydrolysis and dissolution of paint top layer in moist environment and hydrodynamic friction. The term “self-polishing” has been introduced with the development of tributyltin self-polishing copolymer (TBT-SPC)-based antifouling paints (Cavas and Alyuruk 2013). The first use of the term in the marine paints industry is directly related with the working mechanism of TBT-SPC paints. The possible use of TBT acrylate esters in antifouling paints was first suggested by Montermoso and co-workers in 1958. TBT-SPC technology was then patented by Milne and Hails in 1974. The general working mechanism of commercially used TBT-SPC depends on the hydrolysis of the ester bond between the TBT moiety and the carboxyl group of the polymer backbone. TBT acts as a broad-spectrum biocide and can be incorporated into antifouling paints to inhibit fouling on a ship hull up to 5 years. The TBT-SPC paints were so successful that they have been applied in about 70 % of commercial ship. However, the release of toxic TBT into seawater has brought detrimental effects on nontargeted marine organisms and environments. As a result, many governments as well as the International Maritime Organization have restricted, even banned, the use of organotins in antifouling paints. In recent years, many researchers and companies have been devoting many efforts to explore non-tin self-polishing paints as a replacement of TBT-based paints (Lejars et al. 2012).

Cross-References

► [Biofouling](#)

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Biocidal Graphene Oxide Nanosheets

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Biocidal graphene oxide nanosheets are used to provide antimicrobial properties to surfaces. Graphene is a two-dimensional nanomaterial composed of a single atomic layer of sp^2 -bonded carbon atoms. This material came into prominence in 2010 by the awarding of the Nobel Prize in Physics to Andre Geim and Konstantin Novoselov for their research on the properties of graphene. Graphene exhibits excellent electrical, mechanical, optical, and thermal properties that allow its widespread application in photovoltaic devices, transistors, sensors, and electronic visual displays. Graphene possesses the highest theoretical specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) due to its two-dimensional, one-atom-thick structure and thus constitutes an excellent candidate for sorbent material used in water decontamination and gas separation (Zhu et al. 2010). Graphene also possesses good antimicrobial activity and has found several applications for the development of antimicrobial surface coating. Graphene and its oxidized form, graphene oxide, possess a broad-spectrum antimicrobial effect, being effective against gram-positive bacteria, gram-negative bacteria, and

fungi. Cell inactivation by graphene nanomaterials occurs by a combination of cell entrapment, membrane disruption, and the generation of reactive oxygen species, leading to membrane oxidative stress. For all these mechanisms, direct contact between bacterial cells and graphene sheets is required. The antimicrobial potential of graphene nanomaterials is dependent on the physicochemical properties of the material such as sheet size, conductivity, and degree of functionalization.

The biocidal potential of graphene and graphene oxide sheets has been successfully used to impart antimicrobial properties to membranes. For water separation membranes, graphene oxide is usually preferred over reduced graphene due to the more hydrophilic nature of this material. The incorporation of graphene oxide sheets into a membrane for antimicrobial properties may therefore also increase the hydrophilicity of the membrane surface. Graphene oxide sheets can be incorporated in membranes by including the nanomaterials in the polymer solution during fabrication or by post-fabrication surface functionalization. When included in the polymer solution, graphene oxide also contributes to the overall mechanical strength of the membrane and influences its porosity and transport properties (Yu et al. 2013). Since graphene oxide sheets require direct contact for cell inactivation, only the graphene oxide sheets on the membrane surface contribute to the membrane antimicrobial activity. Graphene oxide sheets deeper in the membrane structure do not participate in bacterial inactivation. In order to reduce the amount of material needed to impart antimicrobial properties to a membrane, graphene oxide sheets can be concentrated on the membrane surface via surface functionalization methods. These may involve direct binding of graphene oxide sheets to the membrane using the functional groups of graphene oxide (Perreault et al. 2014), electrostatic interaction between the membrane surface and functionalized graphene oxide (Choi et al. 2013), or the incorporation of the nanomaterial in a polymer composite that is deposited on the membrane surface (Musico et al. 2014). Due to the hydrophilic properties of graphene oxide and the low slip length of water on graphene sheets, the addition of a graphene oxide layer on a membrane surface

for antimicrobial properties do not affect water transport properties.

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Biocompatibility of Membranes

► Membrane Biocompatibility

Biodegradable Membrane

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Biodegradable membranes consist of thin-film-like structures usually applied as separating selective

barriers and support devices. These structures are generally composed of biodegradable polymers, complemented with additives, such as plasticizers, emulsifiers, and cross-linking agents. To be considered biodegradable, all membrane components must be degraded by the action of microorganisms and converted into water, carbon dioxide and/or methane, and new cell biomass.

The wide range of polymers used in the development of biodegradable membranes enables the production of structures with quite diverse properties, finding applications in different areas. It is interesting to note that some of them, beyond being biodegradable, are also biocompatible and/or edible, extending their use to the fields of biomedicine and edible coatings for food products.

Biodegradable polymers obtained by chemical synthesis have been used, for example, in food packaging materials (Siracusa et al. 2008) and medical applications (e.g., fracture fixation, dental orthopedic implants, artificial skin, suture anchors, drug delivery) (Yen et al. 2009; Armentano et al. 2010; Bettahalli et al. 2011). They have also been applied for separation of organic mixtures by pervaporation (Zereshki et al. 2010, 2011).

They include the following:

- (i) Polyglycolic acid (PGA), an aliphatic–aromatic copolymer, which combines the excellent material properties of aromatic polyethylene terephthalate and the biodegradability of aliphatic polyesters. It is produced by a polycondensation reaction of glycol and aliphatic dicarboxylic acids, which may be obtained from renewable resources.
- (ii) Polylactic acid (PLA), a thermoplastic aliphatic polyester obtained from polymerization of the lactic acid monomer produced by microbial fermentation.
- (iii) Polycaprolactone (PCL), a thermoplastic polymer obtained by chemical synthesis using nonrenewable resources (petrochemical derivatives).

Among the biodegradable polymers produced by microbial fermentation, polysaccharides (e.g.,

pullulan, hyaluronan, gellan, GalactoPol, curdlan, bacterial alginate, bacterial cellulose) (Freitas et al. 2011) and polyesters (e.g., polyhydroxyalkanoates) have been applied in films and edible coatings (e.g., pullulan, gellan) (Nieto 2009; Alves et al. 2011). Both microbial polysaccharides and polyesters show a wide range of properties that may be tuned by manipulating the bioreaction conditions. Polyhydroxyalkanoates show a wide range of applications, such as in industry (e.g., packaging, waterproof paperboard), medicine (e.g., bone plates, osteosynthetic materials, surgical sutures, and dressing materials for surgery), and agriculture (e.g., mulch films) (Philip et al. 2007).

The polymers recovered from natural products generally used to produce biodegradable membranes include polysaccharides (e.g., starch, cellulose, pectin, alginate, carrageenan, chitosan) and proteins (e.g., gelatin/collagen, soy protein, gluten). These polymers are widely used to develop edible coatings for food products and biodegradable films intended for food packaging (Nieto 2009). Chitosan, alginate, and collagen are also referred to be applied in tissue engineering (Eisenbarth 2007).

Polysaccharide-based membranes, such as chitosan and sodium alginate, have received much attention for solvent dehydration by pervaporation, due to their good film-forming properties, chemical resistance, and high permselectivity for water (Chapman et al. 2008; Yu et al. 2006).

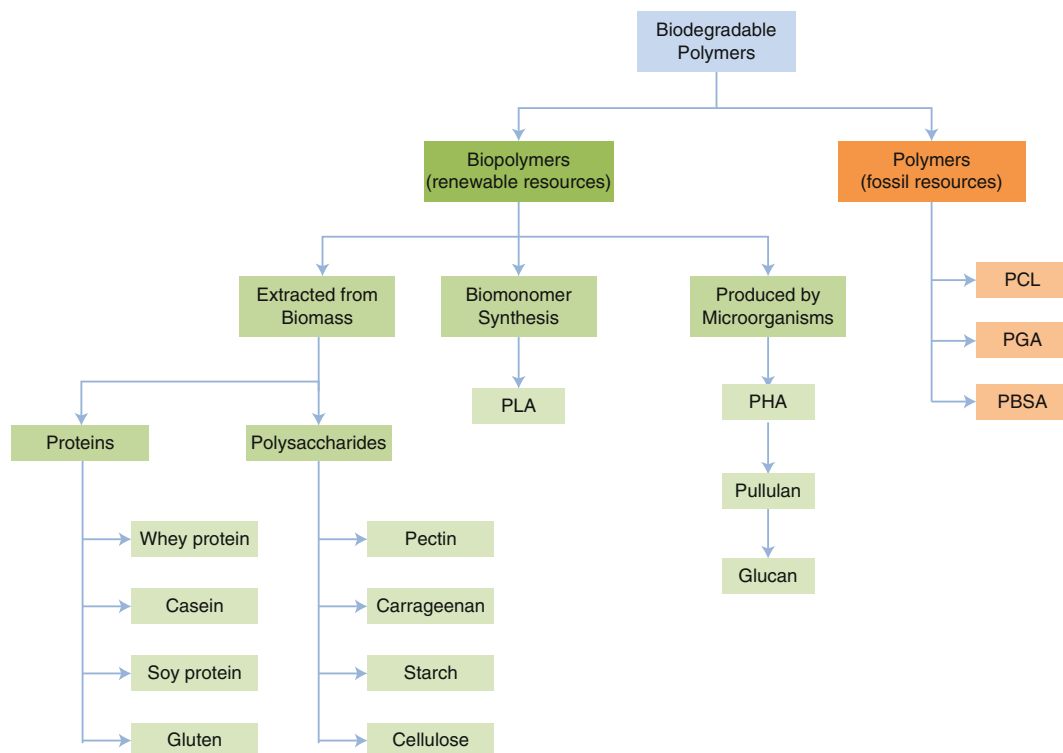
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Biodegradable Organic Matter

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Biodegradable organic matter is organic material, plant, and animal matter with origin in living organisms, which can be converted by the action



Biodegradable Organic Matter, Fig. 1 Biodegradable polymers

of microorganisms to water, carbon dioxide, and/or methane and biomass.

Organic materials can be used to obtain biodegradable polymers which are classified according to the method of production or their source (Fig. 1):

- Polymers directly extracted or removed from biomass such as polysaccharides and proteins
- Polymers produced by classical chemical synthesis starting from renewable bio-based monomers such as polylactic acid (PLA)
- Polymers produced by microorganisms or genetically modified bacteria such as polyhydroxyalkanoates, bacterial cellulose, xanthan, and pullulan (Mensitier et al. 2011)

Polysaccharides are the most abundant macromolecules in the biosphere. These complex carbohydrates constituted of monosaccharides joined together by glycosidic bonds are often one of the

main structural elements of plant and animal exoskeleton (e.g., cellulose, carrageenan, chitin) or have a key role in the plant energy storage (e.g., starch).

Cellulose and starch are of prime interest as biopolymers because of their availability and rather low cost. A variety of polysaccharides and their derivatives, besides starch and cellulose derivatives, have been used as biodegradable membrane-forming matrixes, including alginate, pectin, carrageenan, chitin, and various gums.

Several protein sources have been proposed for the preparation of biopolymers, in particular, cereal proteins which are available in large amounts as by-products arising from agricultural and biofuel processing activities such as ethanol production. These protein-rich products include spent grain from the brewing and distilling industries, cereal bran streams from milling, and protein residues from starch extraction activities (Mensitier et al. 2011).

Microbial biopolymers are naturally synthesized by microorganisms with different functions in the microbial cell, including intracellular carbon or energy storage reserves (e.g., glycogen, polyesters), structural cell wall components (e.g., chitin, β -glucans), and extracellular biopolymers (e.g., exopolysaccharides), often secreted as protective mechanisms in response to environmental conditions (Rehm 2010).

A wide range of agro-food and industrial wastes/by-products have been proposed as alternative substrates for the production of microbial biopolymers, including molasses, cheese whey, palm date syrup, olive mill wastewater (OMW), glycerol by-product from the biodiesel industry, corn-steep liquor, spent malt grains, apple and grape pomaces, citrus peels, peach pulp, used oils, and several acid-hydrolysate wastes (e.g., melon, watermelon, cucumber, tomato, rice), among others (Freitas et al. 2011; Verlinden et al. 2011).

The microbial biopolymers produced include polysaccharides, polyamides, polyesters, and polyanhydrides. Depending on their composition and molecular weight, they have properties ranging from rheology modifiers to bioplastics, which makes them useful in many industrial applications (e.g., agro-food, cosmetics, pharmaceutical, textile) (Rehm 2010).

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Biodegradable Polymer for Membranes

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Synonyms

Biodegradable polymeric membranes; Biopolymers; Polymers for drug delivery; Polymers for tissue engineering

Biodegradable Polymer for Membranes

Membranes made of biodegradable polymers are stable and durable for a specific period of time related to their intended purpose or use in a particular application; after that they break down to result in natural by-products such as gases (CO_2 , N_2), water, biological materials, and inorganic salts.

Biodegradable polymers are naturally and biologically derived or synthetically made and consist of ester, amide, and ether functional groups or bonds.

Naturally and biologically derived polymers are found in nature or created by living organisms. They include *polysaccharides*, like starches found in potatoes or wood, and *proteins*, such as animal-based whey or plant-derived gluten. Polysaccharides consist of glycosidic bonds, between a saccharide and an alcohol; proteins of peptide bonds or amide functional groups between amino acids.

Synthetic materials are man-made. The most important group of synthetic biodegradable polymers is *polyesters* that include *polyhydroxybutyrate* and *polylactic acid*. They can be synthesized in a number of ways including direct condensation of alcohols and acids, ring opening polymerizations (ROP), and metal-catalyzed polymerization reactions. A wide variety of starting materials can be used to synthesize

polyesters, like cyclic dimeric glycolic or lactic acid to form α -hydroxy acids which then polymerize into *poly(α -esters)*, *poly(β -esters)*, and *poly(γ -esters)*. Other synthetic biodegradable polymers are *polyanhydride* and *poly(ester amide)s*, made by condensation, dehydrochlorination, dehydrative coupling, and ROP, and *polyurethanes*, typically synthesized using a diisocyanate, a diol, and a polymer chain extender.

Biopolyesters are produced by both living organisms and synthetic processes. These metal-free processes involve the use of bacterial or enzymatic catalysis, with the benefit of generally regioselective and stereospecific reactions, but with the drawbacks of the high cost of bacteria and enzymes, long reaction times, and products of low molecular weight. Examples of biopolyesters are *poly(glycolic) acid* and *polyhydroxyalkanoates (PHA)* (Zhang et al. 2014).

Membranes made of biodegradable polymers have numerous applications in a variety of fields including medicine, agriculture, and packaging. In the biomedical field, they are of significant interest in applications such as tissue engineering and drug delivery. For these applications biodegradable polymers must answer to specific requirements: they must be nontoxic, capable of maintaining good mechanical integrity until degraded, and capable of controlled rates of degradation. Their products of degradation require also low or negligible toxicity in terms of both local tissue response and systemic immune response.

Biodegradability in tissue engineering is often an essential factor since scaffolds should preferably be absorbed by the surrounding tissues without the necessity of a surgical removal. The rate at which degradation occurs has to coincide as much as possible with the rate of tissue formation: this means that while cells are building their own natural matrix structure around themselves, the scaffold should be able to provide structural integrity within the body and eventually to break down without evoking a foreign body response and leaving the newly formed tissue. They should be

eliminated from the body via natural metabolic pathways. If they are of natural origin, they should be further incorporated in the new forming tissue matrix (Williams 2014). Commonly used natural biodegradable polymers are different proteic derivatives of the extracellular matrix, such as *collagen*, *elastin*, *keratin*, and *fibrin*, and polysaccharidic materials, like *chitosan* and *glycosaminoglycans (GAGs)*. Although they have all proved suitable in terms of cell compatibility, some issues with potential immunogenicity still remains. Among the synthetic materials, *polyurethanes* and *poly(ester amide)s* were initially used for their biocompatibility, durability, and resilience and are only more recently being investigated for their biodegradability. A commonly used synthetic polymer is *polylactic acid (PLA)*, a polyester which degrades within the human body to form lactic acid, a naturally occurring chemical which is easily removed from the body. Similar materials are *polyglycolic acid (PGA)* and *polycaprolactone (PCL)*: their degradation mechanism is similar to that of PLA, but they exhibit, respectively, a faster and a slower rate of degradation compared to PLA. *Polyglycolide*, *polylactide*, *polyhydroxybutyrate*, *chitosan*, *hyaluronic acid*, and *hydrogels* are used in orthopedic applications, such as bone and joint replacement; *poly(2-hydroxyethyl-methacrylate)*, *polyethylene glycol*, *chitosan*, and *hyaluronic acid* are extensively used in the repair of cartilage, ligaments, and tendons (Chiono et al. 2014; Jagur-Grodzinski 2006).

Biodegradable polymeric membranes are of great interest and benefit as drug delivery systems and carriers, where it is critical to target and slowly release the payload drug over time and into a specific site of the body. The polymer slowly degrades into nontoxic and naturally metabolized smaller fragments releasing in the meantime the drug in a controlled fashion. Biodegradable polymers for this purpose must be capable to be formulated for prolonged release of pharmaceutically active compounds. Encapsulating the therapeutic in a polymer and adding targeting agents further decreases the toxicity of

the drug to healthy cells. *Polyanhydrides* are very attractive in drug delivery because they only degrade from the surface and so are able to release the payload drug at a constant rate. *PLA*, *poly(lactic-co-glycolic) acid (PLGA)*, and *PCL* have been used to carry anticancer drugs.

In addition to medicine, biodegradable polymers are often used to reduce the volume of waste in packaging materials derived from petrochemicals. One of the most commonly used biodegradable polymers for packaging purposes is *PLA*, used for a variety of films, such as wrappings, shopping bags, or trash bags, as well as containers, including bottles and cups. Since 2002, *PLA* has been approved by the Food and Drug Administration (FDA) as a safe material to use in all food packaging.

The breakdown of these polymers depends on a variety of factors including the polymer properties and the environment in which they are. Complete *biodegradation* occurs when there are no oligomers or monomers left. Polymer properties that influence degradation are bond type, molecular weight, chain branching, cross-linking, copolymers, crystallinity, hydrophobicity, and solubility. Factors of the surrounding environment, either the atmosphere or the body, include pH, temperature, the presence and concentrations of microorganisms or enzymes, and amount of water. Biodegradable polymers with extremely strong carbon backbones are difficult to break, so degradation often starts from the end groups. Biodegradable polymers with minimal chain branching and cross-linking and with low crystallinity and degree of polymerization often decrease the number of end groups per unit weight but increase their surface area and an easy access for reaction with the degradation initiator. Hydrophobic polymers cannot easily get in contact with water soluble enzymes decreasing their enzyme interaction and degradation. There are two primary mechanisms through which biodegradation can occur. One is through physical decomposition through reactions such as hydrolysis and photodegradation, which can lead to partial or complete degradation. The second mechanistic

route is through biological processes which can be further broken down into aerobic and anaerobic processes. Microorganisms and enzymes that have the ability to break down natural polymers into even simpler units act through oxidation or hydrolysis reactions. Examples of key enzymes include proteases, esterases, glycosidases, and manganese peroxidases.

Cross-References

- [Bioartificial Organs and Tissue](#)
- [Bioartificial Organs, Membrane Operations of](#)
- [Biodegradable Membrane](#)
- [Biodegradation](#)
- [Biopolymers](#)
- [Drug Delivery by Membrane Operations](#)
- [Drug Release](#)
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- [Tissue Engineering, Membrane Operations of](#)

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Biodegradable Polymeric Membranes

- [Biodegradable Polymer for Membranes](#)

Biodegradation

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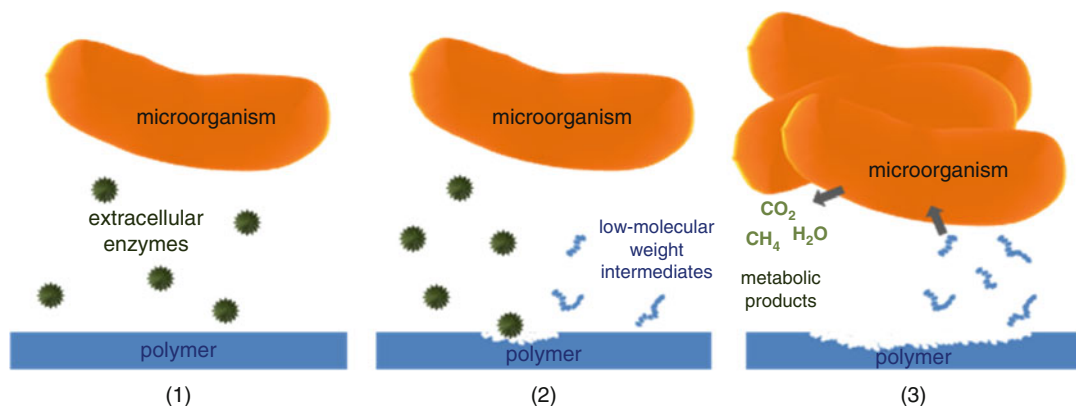
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Biodegradation is the process by which microorganisms (bacteria, fungi, algae) change the chemical structure of a material into naturally occurring metabolic products, ultimately resulting in its conversion into water, carbon dioxide and/or methane, and new cell biomass (Muller 2005). The biodegradation of polymeric materials starts with their depolymerization to generate lower molecular weight intermediates that the microbial cells can then assimilate. The general mechanism of the biodegradation process includes three phases: (1) secretion of extracellular enzymes by the microorganisms; (2) generation of short intermediates by the action of the secreted enzymes; and

(3) conversion of the intermediates into metabolic products (Fig. 1). Water soluble polymers, such as the natural polysaccharides xanthan, alginate, and pectin, are usually more easily degraded, while water insoluble polymers (e.g., polyesters) are more difficult to degrade because the process is heterogeneous. Abiotic processes, such as chemical degradation, thermal hydrolysis, or photodegradation, coexist with the biotic process and often directly induce it by making the materials more easily accessible to the microorganisms. Hence, environmental conditions (e.g., pH, temperature, moisture, salinity, presence/absence of oxygen, nutrient supply) are important factors that influence both the materials themselves and the microbial activity. The complexity of the materials, namely, the structure and composition (single polymer or polymer blends), the presence of additives (e.g., plasticizers), morphology, and crystallinity, are also key issues that directly influence their accessibility to the microbial enzymes.

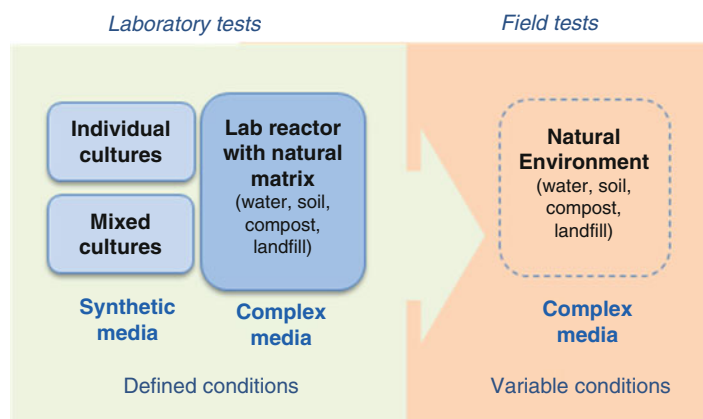
The standardized methods for testing the biodegradability of polymeric materials are based on previously developed methods for low-molecular weight substances. However, they have been modified to consider their higher complexity. Different biodegradability tests can be performed, under both controlled laboratory conditions and also natural environmental conditions. In the laboratory tests, defined environments are created using one of two approaches: (1) inoculation of



Biodegradation, Fig. 1 General mechanism of the biodegradation process: (1) secretion of extracellular enzymes by the microorganisms, (2) generation of short

intermediates by the action of the secreted enzymes, and (3) conversion of the intermediates into metabolic products

Biodegradation,
Fig. 2 Biodegradation
 tests



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synthetic media with individual microorganisms especially selected for a given polymer or with a mixed microbial culture originating, for example, from a wastewater treatment plant or (2) use of complex materials collected from the environment (e.g., water, soil, compost) as the matrix for the tests (Fig. 2).

Some of the standard testing methods include (Shah et al. 2008):

- Visual observations: macroscopic changes, such as roughening of the surface, formation of hole or cracks, changes in color, etc., can be used as a first indication of microbial attack, while more sophisticated observations using, for example, scanning electron microscopy (SEM) or atomic force microscopy (AFM) can be made to obtain more information about the degradation mechanism.
- Weight loss measurements: determination of residual material after being exposed to the biodegradation conditions.
- Changes in mechanical properties and molar mass: properties, such as tensile strength, can be used as indicators of degradation since they are related with the polymer's molar mass.
- CO₂ evolution or O₂ consumption: under aerobic conditions, the microorganisms use O₂ for carbon oxidation, generating CO₂ as one of the major metabolic end product. Hence, CO₂ evolution or O₂ consumption are good indicators of polymer degradation.
- Radio labeling: materials containing a randomly distributed ¹⁴C marker can be exposed

to the microbial environment and the amount of ¹⁴C generated is estimated. It is a high precision test, but labeled materials are not always available and are expensive.

- Clear-zone formation: the polymer is placed in agar plates as very fine particles and inoculated with the microbial culture, being the formation of a clear halo the indication of depolymerization.

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Bioelectrochemical MBR

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Synonyms

Bioelectrochemical membrane bioreactor (MBR);
 Bioelectrochemically assisted membrane bioreac-
 tor; Electrochemical membrane bioreactor; Mem-
 brane bioelectrochemical reactor

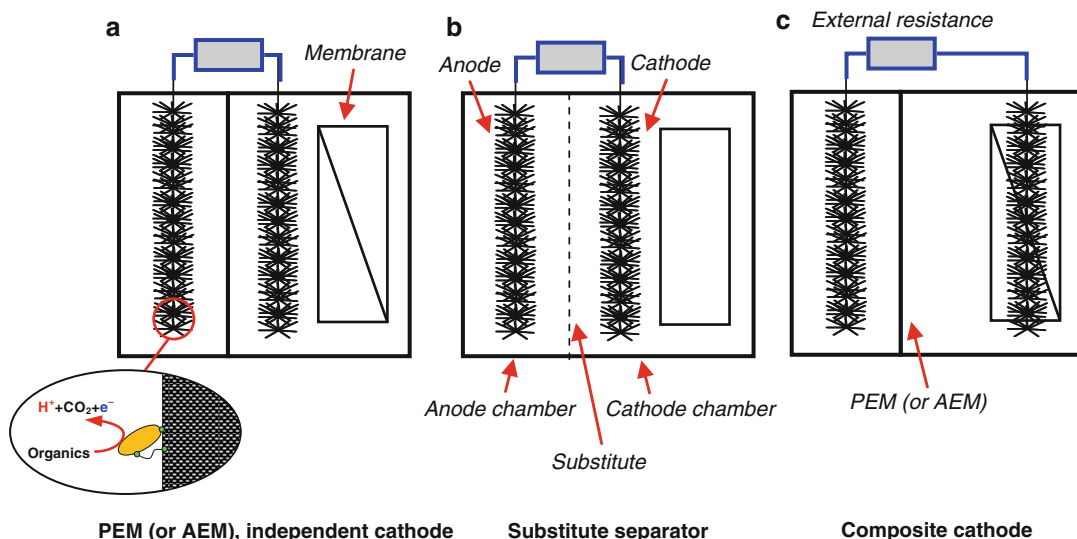
Introduction

Bioelectrochemical MBR is a novel and effective integration of membrane bioreactor process and microbial fuel cell technology, which can recover energy from wastewater and simultaneously harvest clean water for reuse (Wang et al. 2011, 2013a, b; Huang et al. 2014). As shown in Fig. 1, a typical bioelectrochemical MBR consists of an anode chamber (or anaerobic tank) and a cathode chamber (or membrane tank). In the anode chamber, fuel (e.g., organic matter in the influent wastewater) is oxidized by exoelectrogenic bacteria, generating CO_2 , protons, and electrons. Electrons are then transferred to the cathode chamber (or membrane tank) through an external electric circuit, while protons are transferred to the cathode chamber through the separators (e.g., membranes). Electrons and protons are finally consumed on the surface of cathodes to finish the reduction reaction (e.g., oxygen reduction reaction). In these devices, membrane modules are placed in the cathode chamber to enable a sound solid-liquid separation.

Separators with a high conductivity of protons and a low substrate diffusion coefficient are welcome in bioelectrochemical MBRs in order to achieve a selective mass transfer between anode

and cathode chambers (Fig. 1a). Proton exchange membrane (PEM) and anion exchange membrane (AEM) are initially utilized in bioelectrochemical MBRs because these membranes are designed to conduct protons and anions while being impermeable to other reactants (e.g., O_2). Alternatively, substitutes, such as microfiltration membrane, nylon meshes, and perforated plates (Wang et al. 2012), have been also used in bioelectrochemical MBR to separate anode and cathode chambers regarding the construction expenditure (Fig. 1b). As a consequence, coulombic efficiency can be substantially decreased due to unwanted substrate diffusion.

In bioelectrochemical MBRs, anodes are always made of carbon cloth, carbon brush, and carbon paper. The high specific surface area ($100\text{--}2,000\text{ m}^2/\text{g}$) of these materials is conducive for habitation of exoelectrogenic bacteria. Activated carbon can be also used as the anode material, especially in the application of wastewater treatment. Cathodes can be independent or combined with membrane modules. For example, stainless steel mesh has been introduced to constructed cathodes, and the dynamic membrane formed on the cathode subsequently enables the filtration process (Wang et al. 2011, 2013b). Composite cathodes make the reactor more compact,



Bioelectrochemical MBR, Fig. 1 Schematic representation of bioelectrochemical MBRs

which simultaneously alleviates membrane fouling (Liu et al. 2013). Electrochemical MBRs have been also developed by using external power to replace the generated electricity of MFC.

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Bioelectrochemical Membrane Bioreactor (MBR)

- [Bioelectrochemical MBR](#)

Bioelectrochemically Assisted Membrane Bioreactor

- [Bioelectrochemical MBR](#)

Biofabrication

- [Bioartificial Organs and Tissue](#)
- [Tissue Engineering, Membrane Operations of](#)

Biofouling

- [Bacterial Biofilm Formation](#)

Biofuel

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In biofuel production by lipases, membranes are innovative devices used for different tasks. In this respect, they are applied as membrane-immobilized lipases to get the repeated use of expensive biocatalysts in biodiesel fabrication. In this way, the enzyme cost which is being currently the main obstacle for its use in biodiesel production can be overcome by lipase immobilization with the aim of reducing the production cost by reusing the enzymes. Consequently, many research works are currently developed to get efficient, robust, and cost effective membranes able to obtain immobilization of lipases in biodiesel production.

On the other hand, in the production of biodiesel, separation and purification of biodiesel is a critical technology. Conventional technologies used for biodiesel separation, such as gravity settling, decantation, filtration and biodiesel purification by water washing, acid washing, and absorbents have proven to be inefficient. In this respect, membrane reactors are being developed to produce biodiesel from several oils with methanol via enzymatic catalysis as well as by acid- and base-catalysis. Thus, membrane reactors which exhibit intrinsic characteristics of efficiency, operational simplicity and flexibility, relatively high selectivity and permeability, low energy requirements, good stability under a wide spectrum of operating conditions, and easy control have been confirmed in a numerous variety of applications and operations, such as molecular separations, fractionations, concentrations, and purifications within a wide environmental

compatibility. In this respect, novel two-phase membrane reactors seems to be particularly useful in removing unreacted oil from the fatty acid methyl ester (FAME) product yielding a high purity biodiesel. Some research could also be conducted on technologies for biodiesel production by utilizing membrane reactors to handle waste oil in biodiesel production.

Glycerol also causes strong inhibition in the enzymatic methanolysis of triglycerides; therefore glycerol removal by dialysis is carried out using flat sheet membrane modules. Thus, membrane filter devices are useful tools for obtain cleaning of glycerol in biodiesel production. Membrane separation seems to be the most suitable methodology for this purpose. Consequently, the involvement of membrane reactor and separative membrane shows great promise for the separation and purification of biodiesel. Membrane technology are currently being explored and exploited to overcome the difficulties usually encountered in the separation and purification of biodiesel. In this respect, both conventional and most recent membrane technologies used in refining biodiesel are being studied (Atadashi et al. 2011).

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Biofuel Production by Membrane Operations

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In integrated membrane separation for biofuel production, the most essential unit is the separation of product from the raw material mixtures. The membranes are directly combined with the chemical and biochemical conversions to improve

the productivity, biomass conversion efficacy, etc. The significance of these procedures is more than recovery and purification. By in situ removal of one of more products in some cases, they can displace the chemical reaction equilibriums or relieve the toxic effects constraining the conversion. With this feature, the system is named as biofuel production by membrane operations or membrane reactor for biofuel production. The membranes incorporated can be passive ones that only carry out separation of inhibitory product or active ones that conduct catalysis of reactions and separation simultaneously.

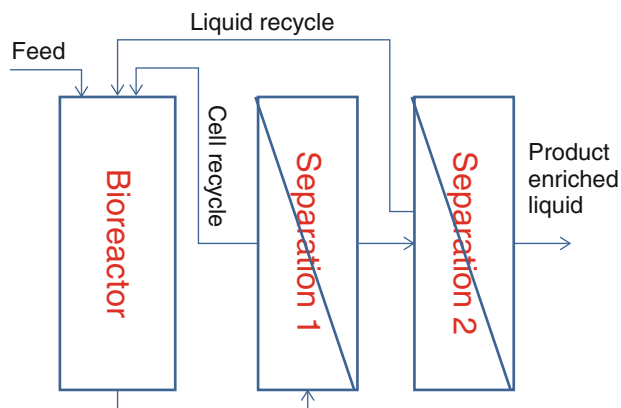
In bioalcohol production through biochemical conversion, the free cell continuous fermentation eliminates downtime, and cell immobilization fermentation increases cell concentration (Quresh and Ezeji 2008). However, the cell washout occurs at high dilution rate in the former. As for the latter, the limitation on substrate supply and toxic product diffusion inactivates a large amount of microbes in the latter. It is difficult for the cells located at the bottom of the biofilm to get enough carbon sources for survival, and the products and other metabolites that have inhibitory effect on the viability of microorganisms encounter great resistance in diffusing away from the cell surroundings. As a solution to these problems reducing the productivity, cell recycle membrane system, which can be called as membrane bioreactor, was developed (Quresh and Ezeji 2008).

The micro-sized cells suspended in broth are rejected by the membrane and recycled back to the reactor as retentate. Figure 1 is the schematic of the cell recycle membrane system. As a result, their concentration can be maintained. The solvents containing the products, on the contrary, pass through the membrane. If the membranes used have selectivity toward the target product, the whole production process will be further improved in economy, as the system is simplified and volume of liquid stream to be treated is reduced.

The bioreactor coupling fermentation and membrane separation has been applied in biobutanol and bioethanol productions. In the acetone/butanol fermentation using *Clostridium acetobutylicum*, the function of microbes is

Biofuel Production by Membrane Operations,

Fig. 1 Schematic of cell recycle membrane system



Separation 1: microfiltration to retain microbial cells.
 Separation 2: membranes that enrich organic component (e.g. product alcohol) at permeate side.

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strongly inhibited by butanol, but acetone has no such toxic effect. Therefore, the purpose to couple the membrane separation is the removal of butanol. The productivity of a fermentation integrating pervaporation to remove butanol from the cultivation medium is up to 65–70 % over the one obtained without membrane separation, and the rate of substrate consumption becomes three times faster. That on-site removal of ethanol by PDMS membrane maintains the ethanol concentration and has also been proved.

Biomass thermochemical conversion technologies such as pyrolysis and gasification are not the most important options at present (Demirbas 2009). As for biogas by anaerobic digestion, gaseous metabolites can be easily taken out by stripping. Membrane separation is more often introduced into reforming steps that generate new products or adjust composition. The steam reforming of methane (CH_4) is an important way to produce syngas and supply hydrogen (H_2) used in fuel cell (Demirbas 2009). It involves two reversible reactions: reforming and water gas shift. The first is endothermic and limited by thermodynamic equilibrium. Therefore, high temperatures are used, making it slow to start up and requiring costly refractory materials. The membrane-based separation proves a cost-effective way requiring less severe operation

conditions. Productivity and conversion could be adjusted by catalyst-embedded membranes which intensify the contact between reactant and catalyst. Bernardo et al. explored CO Serox using catalytic zeolite (Pt/Na-Y) membranes in a continuous flow membrane reactor (Bernardo et al. 2008). Depending on the operating conditions, the catalytic membranes effectively reduced the CO content in H_2 from 10,000 to 10–50 ppm.

Similar to gas reforming mentioned above, transesterification encounters the limit of equilibrium conversion. FAME or glycerol as product should be removed during the reaction in order to shift the equilibrium to the product side. One of the mechanisms used for biodiesel production by membrane reactor is proposed by Dube et al. (2007). The immiscibility of oil and alcohol as well as involvement of various surface forces lead to the formation of an emulsion containing oil droplets suspended in methanol. The transesterification occurs at the surface of the oil droplets. The oil droplets could not pass through the pores of the membrane, whereas the biodiesel product will pass through the membrane pores along with the methanol, glycerol, and catalyst. As a result, the reaction equilibrium is shifted to the product side. Increases in temperature, catalyst concentration, and feedstock flow rate can increase the conversion rate.

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Biofuel Separation by Membranes

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Introduction

The purity of biofuels in forms of gas and liquid generated in biorefinery must meet the in-service requirements (Huang et al. 2008). Several types of membranes have been used for bioalcohols' separation. Pervaporation is molecular-level liquid–liquid separation based on the solution–diffusion mechanism. The polymeric membranes used in pervaporation are essentially dense and inorganic membranes molecularly porous (Jiang and Zhu 2013). The hydrophobic pervaporation recovers the organics from fermentation solution. Polymers such as polydimethylsiloxane (PDMS), ethylene–propylene–diene monomer (EPDM), and polyether block amide (PEBA) exhibit favorable sorption toward organic molecules due to their nonpolar functional groups and minimum diffusion discrimination. Vacuum membrane distillation (VMD) for recovery of bioalcohols uses porous membrane, and the separation is based on vapor–liquid equilibrium and Knudsen/Poiseuille flow (viscous). In comparison with pervaporation using dense membrane, VMD has higher flux but slightly lower separation factor (Urtiaga

et al. 2001). VMD is liable to wetting by alcohols and fouling by microorganisms. Yet another type of membrane is solid (i.e., propylene)–liquid (i.e., oleyl alcohol) combining extraction and pervaporation. It might also be called as membrane contactor. The process exhibited separation of 180 for butanol/water; however, the liquid portion is very unstable. Dehydration by pervaporation is for removing water in the recovered stream so that the fuel specifications could be met. It is a much easier task to achieve high separation factor in dehydration as the diffusion of water molecules is in nature faster than organics. The composite membranes using poly(vinyl alcohol) (PVA) have been commercialized.

In biodiesel production, the removal of glycerol as by-product to fatty acid alkyl esters (FAAE) is very critical. One of the separation approaches uses porous membrane (e.g., MF) (Wang et al. 2009). The immiscibility of glycerol, biodiesel, and soap added lead to the formation of reversed micelle binding glycerol at the hydrophilic site. The micelle is larger than biodiesel molecular and thus retained by the membrane. Membrane separation based on the catalytic pervaporation membrane is investigated in biodiesel production procedure (Guerreiro et al. 2006). Glycerol and methanol are able to form hydrogen bonds with the OH groups in the polymeric membrane and are continuously removed from the products during the reaction.

There exist several approaches for biogas production; they are gasification, pyrolysis, and aerobic digestion. Whichever approach, it is necessary to remove hydrogen sulfide (H_2S), ammonia (NH_3), and siloxane presenting potential damage (e.g., corrosion, erosion, fouling) to devices used in follow-up conversion and pollution to environment. Membrane made of rubbery PDMS has been employed to remove the condensable siloxane (Abatzoglou et al. 2006). In H_2 or CH_4 separation from the other bulk components (mainly CO_2) for various purity requirements, either membranes of molecular sieving or reverse selective membranes relying more on sorption selection, depending on the feed composition, are used (Shao et al. 2009).

The transmembrane flux and separation factor are the key parameters related to the economics of

the process using membrane separation (Vane 2005). For pervaporation, for example, only the permeated components actually undergo liquid–vapor phase change. Therefore higher separation factor means higher energy efficiency. Inorganic membranes generally have better separation performance than polymeric membranes in both hydrophilic and hydrophobic pervaporation. The first large-scale pervaporation plant using tubular-type module of zeolite NaA membrane for dehydration was reported in Japan. In gas separation, to prevent the plasticization by higher condensable molecules (e.g., CO₂) and aging of polymeric membrane, cross-linking of polymer chains via ultraviolet and ion beam radiations, thermal treatment, and chemical modification is applied.

For an active membrane, such as a catalytic one used in selective oxidation of CO, the most important requirements for catalyst are (1) highly selective CO oxidation activity at low temperatures and (2) a wide temperature window for a greater than 99 % conversion of CO (Guerreiro et al. 2006). To achieve high biodiesel yield via catalytic membrane reactor operation, development of cheap and very active heterogeneous catalysts is also necessary. As environment for separation sometimes is very harsh, materials' chemical and mechanical stability become critical to biofuel production by membrane operation. One typical case is biodiesel production using membrane reactor, where viscous nature of feed limits the membrane to tubular ones made of inorganic materials (e.g., Al₂O₃/TiO₂ ceramic) (Park et al. 2004). Additionally, strong acid or base catalysts during biodiesel production also limit the selection to inorganic membranes with high resistance to degradation and corrosion.

The challenges faced by porous membranes, such as MF in sterile separation product from yeast and microbial culture, the high concentration microbes, and correspondingly high level of cell debris, can cause fouling of membrane systems. Similar situation happens in biodiesel transesterification due to oil droplets. Considerable effort is being devoted to developing new membrane modules with improved mass transfer characteristics for microfiltration processes (Reis and Zydney 2001).

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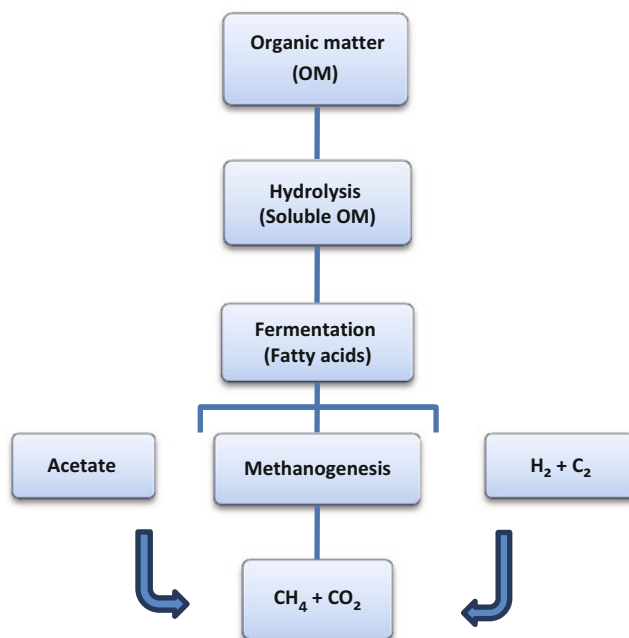
Biogas

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Fossil fuels are still the primary source of energy by preference. However, as fossil fuels become more and more expensive with the possibility of depletion of resources, the quest for alternate sources of energy is gaining attention. In this

Biogas, Fig. 1 Schematic diagram of the anaerobic digestion process for biogas generation (Modified from Basu et al. 2010)



whole situation, anaerobic digestion of biological resources and biological waste could be a promising alternative energy carrier.

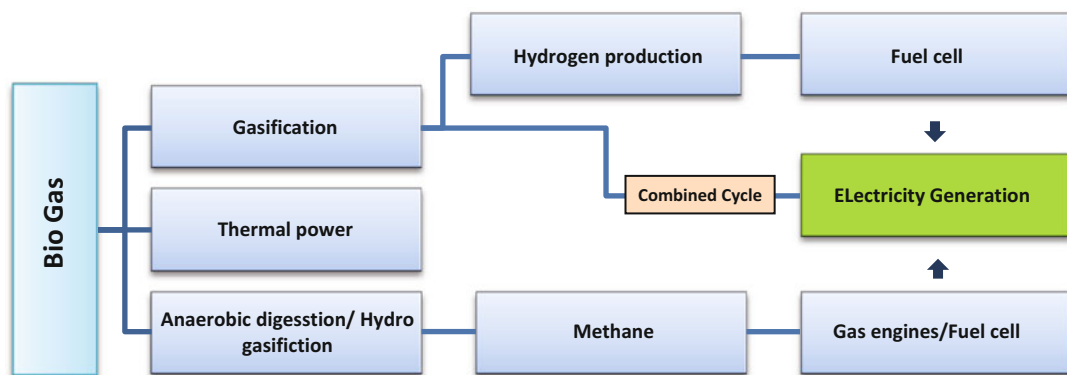
Natural gas normally consists of 90–95 % methane, but in biogas this composition is reduced to 50–65 % making it a low-grade natural gas which is the product of neutral decomposition of organic substance of animal or plant origin due to anaerobic bacterial activity. The plants used for biogas production are normally referred to as anaerobic digesters or anaerobic fermenters. The resources used for biogas production include kitchen waste, dry poultry droppings and animal excrements, remnants of food processing, and slaughterhouse leftovers. Four ingredients needed for biogas production are organic matter, bacteria, anaerobic conditions, and heat. In a controlled reaction system, the gaseous mixture thus produced can contain up to 70 % of biohydrogen and biomethane, respectively, that can be used for commercial applications (Harold 2007).

The anaerobic digestion process can be classified into different sets of complex reactions, as shown in Fig. 1. Production of biohydrogen and

biomethane from organic wastes consists of mainly three steps including hydrolysis, acetogenesis, and methanogenesis. Organic substrates can be converted to biogas by a diverse group of microbes using multienzyme (cellulases, amylases, lipases, proteases, etc.) systems.

Organic material is fed into digesters after grinding to an appropriate size. In the digesters, these substrates are heated and agitated leading to production of biogas which is collected in a biogas container. This gas is fed into an electric generator which produces electricity and heat.

Biohydrogen generated in fermentation processes (e.g., anaerobic fermentation, photofermentation, dark fermentation) has hydrogen and carbon dioxide as major ingredients. On the other hand, biomethane produced by anaerobic digestion of biological wastes has 38–40 % carbon dioxide with smaller amounts of hydrogen sulfide along with trace amounts (ppm) of hydrogen, nitrogen, oxygen, and volatiles with 55–60 % methane as a major part (Rasi et al. 2007). Biogas has a calorific value of 35–44 kJ g⁻¹, which is comparatively higher than other energy resources



Biogas, Fig. 2 Possible applications of biogas as energy resource (Modified from Basu et al. 2010)

like petrol, diesel, or LPG and solid fuels like coal, charcoal wood, etc. Biogas is a potential source of environmentally benign, clean, and cheap alternative energy. However, the presence of incombustible and acid gases, like CO_2 , not only reduces its calorific value, but their corrosive nature restricts its transportation. One of the many trace components includes silicone containing compounds. Commonly occurring siloxanes in biogas are known as volatile methyl siloxanes (VMS) that include cyclic tri-, tetra-, and pentasiloxane, as well as linear di-, tri-, tetrasiloxane. After combustion, undesirable microcrystalline quartz and pentasiloxane are produced as they cause the wear & tear of engines and turbines. Purified biogas can be used as a feed to fuel cells or for domestic applications and power generation. Figure 2 represents the possible applications of biogas (Basu et al. 2010).

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Biogas Production

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Biogas mainly consists of methane and carbon dioxide and is saturated with water. Minor components such as hydrogen sulfide and ammonia are also present in the raw biogas. Biogas is produced in on-farm fermenters in the agricultural production where crops or manure are digested, in sewage plants, and by landfills. It can either be used to operate a combined heat and power engine on site or as natural gas substitute when upgrading the raw biogas. Using a combined heat and power engine (CHP) can be efficient if the produced heat is utilized (e.g., district heating). However, the heat can often not be used. Hence, upgrading the biogas and injecting the purified gas to the natural gas grid is an interesting alternative compared to onsite electricity production by CHPs. In order to upgrade biogas carbon dioxide, hydrogen sulfide and water vapor have to be removed prior to grid injection. The term upgrading particularly refers to the removal of carbon dioxide as it is the main gas component to be removed from the methane-rich raw biogas. The upgraded biogas can be utilized as a natural gas substitute. Hence, it can

Biogas Production, Table 1 Biogas upgrading technologies

Technology	Material	Process	Ref.
Chemical absorption	Diethanolamine	DEA scrubbing	Hofmann and Plaettner (2006)
	Methyldiethanolamine	MDEA scrubbing	Hofmann and Plaettner (2006)
	Monoethanolamine	MEA scrubbing	Hofmann and Plaettner (2006)
Physical absorption	Methanol	Rectisol	Hofmann and Plaettner (2006)
	Polyethylene glycol dimethyl ether	Selexol	Hofmann and Plaettner (2006)
	Polyglycol dimethyl ether	Genosorb	Urban et al. (2007–2008)
	Water	Pressurized water scrubbing	Hofmann and Plaettner (2006)
Adsorption	Activated carbon	Pressure swing adsorption	Hofmann and Plaettner (2006)
	Molecular sieves	Pressure swing adsorption	Hofmann and Plaettner (2006)
Membranes	Cellulose acetate	Gas permeation	Scholz et al. (2013)
	Ethyl cellulose	Gas permeation	Scholz et al. (2013)
	Polycarbonate	Gas permeation	Scholz et al. (2013)
	Polyimide	Gas permeation	Scholz et al. (2013)
	Polymethyldisiloxane	Gas permeation	Scholz et al. (2013)
	Polymethylpentene	Gas permeation	Scholz et al. (2013)
	Polyphenylene oxide	Gas permeation	Scholz et al. (2013)
	Polysulfone	Gas permeation	Scholz et al. (2013)

drive large-scale, central gas turbines or combined heat and power cycles in which the produced heat can be used. In addition, upgraded biogas can be utilized as fuel for vehicles or it can be used as feedstock for the chemical synthesis (Baerns et al. 2006).

Various technologies exist to upgrade biogas (Hofmann and Plaettner 2006). Physical and chemical absorption and adsorption are well-established technologies to upgrade biogas. Recently, gas permeation membranes became important in biogas upgrading (Scholz et al. 2013), as gas permeation processes are energy efficient, easy to handle, and robust, which is important in the on-farm operation. In principle, cryogenic separation could also be applied to separate methane and carbon dioxide, but due to the low raw gas flow rates (typically less than 2,000 m³ (STP)/h), it is uneconomical. Recently, a membrane cryogenic process was designed which is able to compete with

established technologies such as amine scrubbing (Pentair 2013) (Table 1).

There is no international standard on the gas specifications to be supplied to the natural gas grid. In general, the methane content should be higher than 96 %. Often the gas has to be supplied at elevated pressures (e.g., >10 bar). The tolerable hydrogen sulfide levels vary also depending on the country the biogas plant is operated in. The electrical and thermal energy demand to drive the upgrading process is typically in the range of 0.15–0.25 kWh/m³ (STP) and 0.3–0.8 kWh/m³ (STP), respectively. Methane recoveries, which are the ratio of the methane flow rate of the product gas to the methane flow rate of the feed gas, of more than 99 % should be achieved to minimize the environmental impact and to enhance the process economics. However, the product gas requirements have to be analyzed for each individual biogas upgrading plant.

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Biogas Recovery

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The constant increase in energy demand, coupled with the depletion of fossil fuels, is a concern that cannot be ignored in the industrial and highly populated world of today (Basu et al. 2010). Biogas production is a very promising source of renewable energy that still offers further exploitation of its potential (Scholz et al. 2013). Essentially, microbially controlled biogas production is an already existing part of the global carbon cycle, releasing an estimated 590–800 million tons of methane to the atmosphere (Bond and Templeton 2011). Current biogas recovery systems seek to exploit these processes in order to produce energy from sewage wastewater, animal manure, crop straws, or mixed agricultural wastes (Chen et al. 2012; Rasi et al. 2011). Usually, a system for biogas recovery consists of four components: a collection system which helps transfer the biogas source to the anaerobic digester, the anaerobic

digester in which the methane production takes place, a biogas collection system providing piping of biogas to a combustion device, and a gas use device where biogas is combusted to produce heat or electricity (Agstar 2011). Alternatively, the produced biogas can be used on site as fuel for automobiles or can be injected in the natural gas grid. In this case, the gas must be upgraded to natural gas standards, namely, 98 % methane content (AEBIOM 2009).

Although the composition of biogas varies significantly depending on many factors such as the type of digester, the average values are reported to range between 50 % and 70 % methane and 30–50 % carbon dioxide, as well as hydrogen sulfide, sulfur compounds, siloxanes, and aromatic and halogenated compounds (Rasi et al. 2007). Upgrading (purification) of biogas is highly beneficial in terms of increasing the amount of methane per unit volume of biogas, which equals an increase in its calorific value. In addition to the obvious need for removal of carbon dioxide as the major pollutant, the trace compounds have the potential to trigger ozone depletion and the greenhouse effect, reduce the quality of local air due to formation of volatile organic compounds (VOCs), and so on. Moreover, sulfur compounds corrode pipelines and combustion engines, while silicon compounds oxidize and are deposited on engine parts (Rasi et al. 2007). Currently, biogas upgrading is largely achieved through amine scrubbing where carbon dioxide is absorbed into an amine solution, water scrubbing where carbon dioxide is absorbed to water at elevated pressures, and pressure swing adsorption where pressure of the gas mixture is changed to induce adsorption and desorption of one gas species. These technologies are in general more energy intensive and polluting than membrane technology (Basu et al. 2010; AEBIOM 2009; Scholz et al. 2013). Polymeric membranes have gained a share in the separations market, as opposed to the inorganic membranes which are expensive and brittle. Some commercial polymeric membranes such as SEPAREX (cellulose acetate) of UOP and polydimethyl siloxane (PDMS) have

already proven or were reported to operate successfully in separation of carbon dioxide or siloxanes and VOCs, respectively. However, the separation of hydrogen sulfide still remains a difficult and interesting issue for membrane research. Mixed matrix membranes composed of inorganic particles distributed throughout a polymeric matrix are promising alternatives thoroughly investigated for these separations (Basu et al. 2010).

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- industrial waste. The composition of biogas varies from the origin of the anaerobic digestion process, and the main components are methane (CH₄) and carbon dioxide (CO₂) as shown in Table 1 (Rasi et al. 2007). Biogas has a very high-energy potential due to the presence of methane (CH₄) and thus is a great source for renewable energy production, which can be used for heating, combined heat and power (CHP) generation, vehicle fuel, fuel cell, and substitute natural gas. Depending on the different end uses, the specific biogas treatment should be executed. For the applications as vehicle fuels and natural gas grid injection, CO₂ should be removed from the raw biogas, i.e., biogas upgrading, to reduce the corrosion caused by the acid gases and increase the Wobbe index which is directly proportion to the methane concentration. However, biogas upgrading process will add extra costs into the biogas production. Thus, an optimized upgrading technology in terms of low energy consumption and high efficiency should be developed to reduce the biogas production cost. Moreover, the minimum emission of CH₄ should also be addressed since methane has a greenhouse effect of around 23 times higher than that of CO₂.

Different techniques such as pressure swing adsorption (PSA), physical absorption (e.g., water scrubbing), chemical absorption (e.g., amines), and membrane system have been investigated for biogas upgrading. The choice of a suitable technology is mainly dependent on the specific condition at a plant, such as availability of low price for heating, electricity, and water, as well as the amount of gas to be handled. Today, most of biogas upgrading plants in Sweden are still using PSA even though the methane content in the upgraded gas is low (96 %) and methane loss is quite high (3–10 %), while some plants using water scrubbing technique will additionally produce a lot of wastewater, and electricity consumption is also quite high. Membrane system could be favorable for biogas upgrading due to a series of advantages including the safety and simplicity of the operation and easy maintenance without any hazardous chemicals (Makaruk et al. 2010). Figure 1 shows a schematic diagram of membrane system for biogas upgrading.

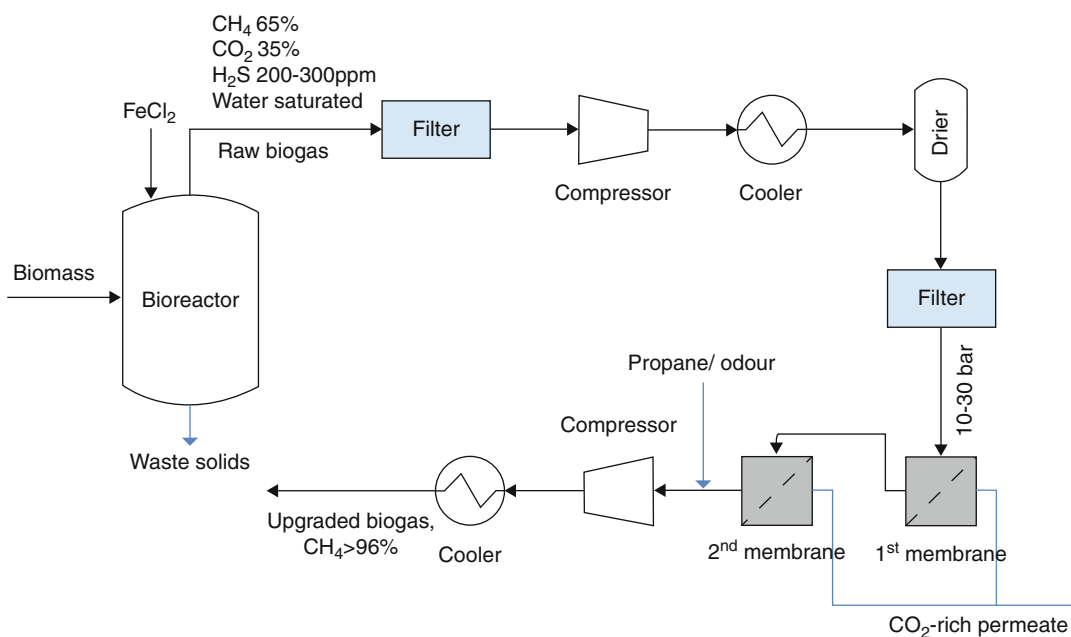
Biogas Upgrading

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Biogas is produced in anaerobic digesters from biodegradable wastes such as sewage sludge, manure, organic fraction of household, and

Biogas Upgrading, Table 1 Typical gas composition from different sources (Rasi et al. 2007)

Process	Composition (vol, %)					H ₂ S/SO ₂ (ppm)
	CO ₂	CH ₄	N ₂	O ₂	H ₂ O	
Farm biogas plant	37–38	55–58	<2	<1	4–7	32–169
Sewage digester	38.6	57.8	3.7	0	4–7	62.9
Landfill	37–41	47–57	<1	<1	4–7	36–115

**Biogas Upgrading, Fig. 1** A schematic diagram for biogas upgrading process by membrane systems

As illustrated in the above flow sheet, H₂S and water vapor must be removed before feeding into the membrane system. Compression of gas may vary depending on whether it goes to natural gas grid (<80 bar) or will be used for vehicle fuel (~200 bar). The main challenge of a membrane system is the pretreatment of biogas to protect the membrane materials, especially for the biogas produced from the sewage treatment plants and landfill sites where it usually have a lot of malicious gas components. Polyvinyl amine (PVA)/polyvinyl alcohol (PVA) blend fixed-site-carrier (FSC) membranes for biogas upgrading have been investigated by Deng et al. (Deng and Hägg 2010). Their results indicated that a membrane process with a CH₄ recovery of 99 % at a low operation cost could be designed to achieve the

specification of natural gas network distribution, which makes this environmentally friendly technology more competitive compared to the other conventional technologies currently used. Makaruk et al. pointed out that membrane system provides enough flexibility for heat integration within biogas plants (Makaruk et al. 2010), and the expected energy requirement for a single-produced cubic meter of natural gas substitute is estimated to be around 0.3 kWh, which is close to the values reported in an industrial scale demonstrator for membrane biogas upgrading plant at Bruck an der Leitha in Austria (Miltner et al. 2008). Moreover, a new carbon membrane company MemfoACT (<http://www.memforact.no>) was launched in 2008 in Norway, which mainly focuses on the biogas upgrading using

their patented hollow fiber carbon molecular sieve membranes. Their contributions could promote to bring this technology into the commercial application in the near future.

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Biogas Upgrading by Membrane Processes

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Biogas upgrading, which is the removal of carbon dioxide from a methane-rich raw biogas, can be accomplished using membranes. Gas permeation membranes or membrane contactors can be applied to remove carbon dioxide. Membrane contactors are still under investigation, while gas permeation modules are applied in commercial biogas upgrading plants (Scholz et al. 2013). In principle, organic as well as inorganic membrane materials have excellent selectivities to separate carbon dioxide and methane. However, Baker (2001) reports that only a limited number of membrane materials are commercially available as membrane modules, and all these membranes are made out of polymers. For commercial polymeric membranes, carbon dioxide permeates faster

through the membrane than methane. Thus, the methane-rich product gas is supplied on the retentate side of the membrane stages.

Some commercially available membrane materials have selectivities of as high as 60 (Scholz et al. 2013). However, by applying these membranes in a single-stage gas permeation process, significant methane losses are observed in order to achieve the required methane purity of 96 % (Rautenbach and Welsch 1993). Hence, the trade-off between methane purity and methane recovery cannot be overcome. Therefore, multi-stage gas permeation processes are required to produce a product gas with methane purities of more than 96 % while simultaneously providing methane recoveries of more than 99 %. To design an upgrading process with high methane recoveries is particularly important as the methane recovery determines the profitability of the biogas upgrading plant and competing upgrading processes such as amine scrubbing or pressure swing adsorption show high methane recoveries.

The driving force to operate the gas permeation process can either be provided by a feed-side compression or by a permeate-side vacuum pump. As the carbon dioxide content in the raw gas can be as high as 50 % and the methane-rich product gas should be provided at elevated pressures, the compression prior to the gas permeation system is preferred over a system operating with subambient pressure on the permeate side. Here, the compressor provides both the driving force for the permeation of carbon dioxide and the elevated pressure of the product gas for natural gas grid injection.

Gas permeation membranes can be combined with conventional gas separation technologies in membrane hybrid processes. Recently, a membrane cryogenic process was reported, which has high methane recoveries (Pentair 2013). In this particular process, the gas permeation stage is applied to provide the methane-rich product gas. Since the permeate stream of the membrane stage contains significant quantities of methane, the permeate stream is compressed up to 20 bar and fed to a cryogenic separation unit, which operates at –24 °C. Here, the carbon dioxide fraction is

liquefied and a methane recovery of 100 % can be obtained.

Another option to upgrade biogas is to use a single-stage membrane process and to supply the upgraded biogas in one step. The permeate of the membrane stage, which contains significant amounts of methane, is combusted in a combined heat and power engine (Makaruk et al. 2010). The combined heat and power engine requires at least a methane level of 30 % so that raw biogas can be mixed with the permeate stream to adjust the methane level. By applying this particular process design, the electrical energy demand to drive the upgrading process can be provided by the gas engine. However, the produced heat cannot be used efficiently.

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Biohybrid Artificial Liver (BAL)

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A biohybrid artificial liver (BAL) is a bioartificial device which consists of functional liver cells supported by an artificial cell culture material. It incorporates hepatocytes into a bioreactor in which the cells are immobilized, cultured, and induced to perform the hepatic functions by processing the

blood or plasma of liver failure patients. BAL provides temporary support for patients waiting for an allogeneic liver transplant, and since the liver can regenerate, the temporary support provided by BAL may allow time for liver regeneration.

The bioreactor is an important component of BAL, because it determines the viability and function of the hepatocytes within it. A successful and clinically effective bioreactor should mimic the structure of the liver and provide an in vivo-like microenvironment for the growth of hepatocytes, thereby maintaining the cells' viability and function to the maximum extent. The important issues are the choice of cell sources and the design of the bioreactor (Ding and Shi 2011). The cell sources provide liver-specific functions, such as detoxification, drug metabolism, and protein synthesis, while the bioreactors maintain the viability and function of cells. More efforts are now underway in search for the best cell resource and best design of bioreactors.

Considering the several functions that the liver performs, the bioreactor for BAL devices has to ensure the rapid detoxification of neural and hepatic toxins, the return of liver-specific hepatotrophic factors, as well as liver-specific coagulation factors, back into patient's blood, and the maintenance of liver cell detoxification and synthetic functions until liver tissue regeneration or organ transplantation.

One of the most promising bioreactors is the membrane bioreactor. Polymeric membranes in flat and hollow fiber configuration with different morphology and chemical–physical properties have been used in BAL devices (De Bartolo and Bader 2001; Kamlot et al., 1996; Kasuya and Tanishita 2012). Most of the extracorporeal BALs have not only used cellulose and polysulfone derivatives but also native and modified polypropylene membranes. Morphological (e.g., pore size, pore size distribution, and roughness) and physicochemical membrane properties (e.g., surface charge, wettability, and surface free energy) affect all the adhesion and metabolic functions of hepatocytes.

Hepatocytes have been cultured in membrane bioreactors in different configurations: between flat sheet membranes in a sandwich configuration; in the lumen of hollow fiber membranes entrapped

in a collagen layer; in the shell of hollow fiber membranes in monolayer, aggregate, or spheroid structure and attached to microcarriers; in a network of hollow fiber membranes with different functions; in a spirally wound device in which hollow fibers are used to provide oxygen to the cells; in multibore capillaries; microencapsulated and in an oxygen-permeable membrane rotating system under microgravity conditions.

Several designs of BAL devices that are different in configuration, cell source, and culture technique have currently undergone clinical trials (Morelli et al. 2010).

Cross-References

► [Bioartificial Liver](#)

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Biohybrid Artificial Liver (BAL) Systems

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A biohybrid artificial liver (BAL) system is an artificial extracorporeal supportive device which

represents an important therapeutic strategy for patients with acute liver failure.

Generally, a BAL system consists of functional liver cells supported by an artificial cell culture material. In particular, it incorporates hepatocytes into a bioreactor in which the cells are immobilized, cultured, and induced to perform the hepatic functions by processing the blood or plasma of liver failure patients. The BAL system acts as a bridge for the patients until a donor organ is available for transplantation or until liver regeneration. The development of a BAL system involves many design considerations. It must provide (1) an adhesion support to the cells; (2) adequate mass transfer of oxygen, nutrients, and toxic substances from the blood or plasma of patients to the cell compartments and proteins, catabolites, and other specific compounds produced by cells from the cell compartment to the blood or plasma; (3) immunoprotection of cells; and (4) biocompatibility. BAL devices are classified by the cell source, the type of culture system for the hepatocytes, and the configuration of the bioreactor.

Several BAL systems have been evaluated preclinically in in vitro experiments and in large animal models of liver failure (Morelli et al. 2010). Currently, different types of BAL devices are in various stages of clinical evaluation, and some of them are listed in Table 1 (van de Kerkhove et al. 2004).

Many of these devices use hollow fiber membranes (HFMs) as supports for the cultured hepatocytes and as immunoselective barriers between the plasma of the patients and the hepatocytes used in the bioreactor. Membranes also permit the transport of nutrients and metabolites to cells and the transport of catabolites and specific metabolic products to the blood. In the membrane bioreactors, mass transfer is determined by the molecular weight cutoff (MWCO) or pore diameter of the membrane and occurs by diffusion and/or convection in response to existing transmembrane concentration or pressure gradients. Most of the bioreactors for BAL systems use membranes with MWCO ranging from 70 to 100 kDa that allow the transport of serum albumin but exclude proteins with high MW such as immunoglobulins and cells.

Biohybrid Artificial Liver (BAL) Systems, Table 1 Membrane BAL systems in clinical evaluation

BAL system	Bioreactor configuration	Membrane	References
Kiil dialyzer bioartificial liver	Plate	Cellulose	Matsumura et al. (1987)
ELAD	Hollow fiber	Cellulose acetate	Sussman et al. (1992)
Amphioxus Cell Technology			
LLS	Hollow fiber	Polyamide	Gerlach et al. (1994)
Charite, Humboldt University, Germany		Polyethersulfone	
		Polypropylene	
HepatAssist	Hollow fiber	Polysulfone	Demetriou et al. (1995)
Circe Biomedical			
AMC-BAL	Spirally wound	Nonwoven polyester matrix, polypropylene	Flendrig et al. (1997)
University of Amsterdam			
BLSS	Hollow fiber	Cellulose acetate	Patzer et al. (2002)
Excorp Medical Inc.			
BAL TECA Corp.	Hollow fiber	Polysulfone	Ding et al. (2003)

One of the first clinical devices using HFMs was developed by Sussman and coworkers, namely, the extracorporeal liver-assist device (ELAD) in which the human hepatocytes were located outside the hollow fiber and blood flows through the lumen of the hollow fibers. This device was commercialized by Amphioxus Cell Technologies (Sussman et al. 1992). HepatAssist Circe Biomedical is the most clinically advanced system of its kind. It is an extracorporeal cell-based bioartificial liver device, based on the use of an open membrane hollow fiber bioreactor (Demetriou et al. 1995). In this system, hepatocytes are loaded into the extracapillary space, and the patient's plasma flows through the capillary lumina of membranes. A more complex system is the liver support system (LSS) or the modular extracorporeal liver system (MELS) which consists of a bioreactor with four interwoven independent capillary membrane systems that serve different functions (Gerlach et al. 1994). The BLSS is a hollow fiber device that uses porcine hepatocytes embedded in a collagen matrix (Patzer et al. 2002). The Academic Medical Center Bioartificial Liver (AMC-BAL) developed by Flendrig et al. uses a three-dimensional, spirally wound, nonwoven polyester matrix for hepatocyte attachment with integrated hollow fibers for oxygen delivery to the cells (Flendrig et al. 1997). Another BAL system that is currently in clinical

testing is a bioreactor from TECA Corp. in which a polysulfone membrane compartmentalizes porcine hepatocytes (Ding et al. 2003).

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Biohybrid Artificial Liver Systems

► Bioartificial Liver Support System (BLSS)

Biohybrid Membrane Systems

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Biohybrid membrane systems are engineered systems based on the combination of biological units, cells, or tissues, immobilized on an artificial structure, the membrane. In these systems, membranes act as instructive materials which are capable of supporting tissue/organ formation. Cells have to make an intimate contact with the surface of the membrane but also to develop close cell-cell connections, which is a precondition for their survival and high functional activity.

Among polymeric materials, membranes in flat and hollow fiber configuration are the most attractive in the use of biohybrid systems for their characteristics of stability, biocompatibility, and selective permeability. Polymeric membranes could mimic the extracellular matrix with which cells interact allowing the organization of the cells into a three-dimensional architecture. The membranes are able to modulate the adhesion, proliferation, and differentiation of cells which are fundamental processes for tissue regeneration by governing the mass transfer of molecules that generate a precisely controlled microenvironment

that mimic the specific features of in vivo environments.

Biohybrid membrane systems are successfully applied in the field of tissue engineering and regenerative medicine (Morelli et al. 2009). For the development of functional biohybrid membrane systems, a number of issues need to be addressed: morphological, physicochemical, mechanical, and transport properties of the membrane, the optimal density of immobilized cells, the interaction of cells with the membrane, the differentiation of cells, as well as the maintenance of viability and metabolic functions in vitro membrane constructs.

Different types of biohybrid membrane systems have been proposed for the reconstruction and/or regeneration of many organs and tissues (e.g., the pancreas, liver, kidney, skin, and bone Scharp et al. 1994; Saito et al. 2006; De Bartolo et al. 2009; Ding and Shi 2011; Gentile et al. 2011).

Currently, biohybrid membrane systems are also developed for the creation of a biomimetic microenvironment for neural tissue engineering since they may be used for the in vitro simulation of human brain functions. Semipermeable hollow fiber membranes are widely used as guidance channels in promoting in vitro and in vivo neuronal regeneration (Zhang et al. 2005; Morelli et al. 2010, 2012).

Generally, biohybrid membrane systems could not only have a role in the replacement of injured organ or tissue but also accelerate the development of new drugs that may cure patients as an alternative to animal experimentation.

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- Tissue Engineering, Membrane Operations of

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Bioinspired Membranes

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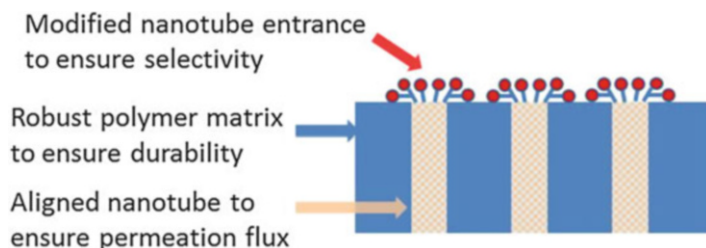
Bioinspired membrane can be thought of as a comprehensive name for a big family of artificial membranes of which the design originality arises from biological phenomena and principles in nature. Compared with biomimetic membrane, bioinspired membrane is a much broader term (Rawlings et al. 2012), because a bioinspired membrane does not necessarily employ biological membrane or biologically occurring thin film as

the archetype. On the one hand, the membrane materials (organic, inorganic, or organic-inorganic hybrid) can be synthesized by borrowing the fundamental principles of the materials processing in nature. On the other hand, the advancement in any branch of biological materials science related to structure, function, and structure-function relationships can be employed and incorporated to rationally design the structure or function of bioinspired membrane. As a result, the membrane preparation is usually conducted under very mild conditions (aqueous solution, ambient temperature and pressure, neutral or near neutral pH, etc.), the membrane materials are often easily available and biodegradable, the membrane structure can be finely tuned, and the membrane often displays multiple functions and high application efficiency. To some extent, the bioinspired membrane can be viewed as next-generation membrane.

At present, several bioinspired platform techniques based on fascinating biochemistry and biology have been developed. For example, inspired by formation process of biosilica, a platform technique called “biomineralization” or “biomimetic mineralization” was developed to fabricate polymer-inorganic nanohybrid membrane (Pan et al. 2010). By using biomolecules as catalyst and/or template, silica nanoparticles were in situ generated and well dispersed in a polymer matrix, and the as-prepared hybrid membrane synergistically combined the advantages of two components. Another platform technique example is “bioadhesion” or “biomimetic adhesion.” This technique originated from mussel-inspired catecholic chemistry, which was successfully utilized to construct ultrathin and stable active layer of dense composite membrane (Li et al. 2009). The other techniques are mostly based on self-assembly, in particular layer-by-layer (LBL) assembly. LBL assembly technique provides a powerful platform to manipulate multiple interactions, such as covalent bond, hydrogen bonding, charge transfer, hydrophobic, host-guest, and coordination bond interactions (Matsusaki et al. 2012), so as to prepare membrane with precisely tailored nanostructures (i.e., thickness, free volume, hydrophilicity, etc.).

Bioinspired Membranes,

Fig. 1 Concept of nanotube-based hierarchically structured membrane with durable high permeability and selectivity



Future effort on this type of bioinspired membrane may turn to improving the fundamental mechanism and extending the application fields. Of course, new bioinspired platform techniques will be continuously explored.

Selective transport properties and the corresponding membrane structures are another major concern in bioinspired membrane realm. In biology, the most effective membrane-mediated separation/transport processes often involve complex, nonplanar articulations of structure that are highly optimized to support the multiple functions. Inspired by the hierarchical structures in biology, rational design and synthesis hierarchical structures within membranes may offer immense opportunities for efficient molecular/ion sieving processes. For example, nanotubes have been utilized to mimic biological channels for rapid and selective molecule transport. With the aid of nanotubes, an ideal concept of vertically aligned biomimetic channels within a membrane matrix have been proposed and shown in Fig. 1, where membrane permeability, selectivity, and durability are individually manipulated by the highly permeable nanopores, the entrance chemistry of the nanotube, and the robust nonporous filling matrix. Here, the aligned nanotubes are extremely like the channel proteins inserted through cell membranes. This concept has partially come true recently (Xu et al. 2011), and it requires much more efforts to fulfill all the potentials of this concept. Also, many block copolymers have been designed to mimic the hydrophilic-hydrophobic mosaic structure of biomembrane for antifouling (Chen et al. 2011). Moreover, many efforts have been dedicated to mimicking the proton pump and ion channel so as to accelerate proton transport (Wang et al. 2012; Sharma et al. 2010). In addition to selective

transport properties, intelligent properties of membranes show great promise in membrane science and technology (Tokarev and Minko 2010). For instance, self-healing membrane, self-cleaning membrane, and many sorts of stimuli-responsive membranes have been reported (Chen et al. 2011; Wang et al. 2011b; Capadona et al. 2008; Tokarev and Minko 2010). Such smart behaviors can endow the membrane with ultra-high stability, switchable permeation flux, alternative driving force, etc. Other properties, such as mechanical strength, interface adhesion, water retention, etc., have been successfully reinforced by learning from nature (Zeng et al. 2010; Ma et al. 2010; Wang et al. 2011a). Breakthroughs in understanding how a living system works and exploring new inspiration source will ensure the sustainable development of bioinspired membrane.

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Biointerface

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Synonyms

Biorecognition substrate

A biointerface is an interface between biological material (e.g., cells, tissue) and a (commonly) synthetic substrate. Biointerfaces call for advanced design and preparation in order to match the sophisticated (bio) recognition ability of biological systems. Specifically this requires combined topographic, chemical, and viscoelastic patterns on surfaces to match proteins at the nm scale and cells at the micrometer scale (Kasemo 2002).

Biointerfaces are typically used in the fields of immunology, surgery, pathology, pharmacology, and many others either for the proliferation of cells for further application or investigative study or as a platform for cell manipulation. These studies have become even more topical upon completion of the human genome project, which has set the formidable challenge of elucidating the function of the vast amount of genomic information within the genotype of an individual.

A potential medical application of a biointerface is in the ex situ growth of skin/bone/organ tissue for subsequent transplantation. For example, burn victims can have their own replacement skin grown in a laboratory via the proliferation of their own epidermal cells upon a biointerface in a laboratory. Biointerfaces themselves can potentially be installed in situ to assist in cell regeneration, such as after surgery. For this purpose, biodegradable biointerfaces are of particular interest as they perform their function of assisting cell regeneration and are then degraded naturally into nontoxic products which are then excreted (Hook et al. 2006).

The scientific study of cells is important to improve fundamental understanding of their working process. Biointerfaces are often used as experimental platforms to study various properties of cells. For instance, neuronal cells are electrically excitable cell that processes and transmits information through electrical and chemical signals. The growth of these cells on specially designed biointerfaces has allowed scientists to directly investigate their signal transmission process (Robinson et al. 2012).

The fabrication of various biointerfaces is of particular interest for stem cell research. Stem cells can differentiate into a variety of different

cell types depending upon their environment (Pittenger et al. 1999). Therefore, the careful design of particular biointerfaces can promote stem cell differentiation into a desired cell type. For example, stem cells adsorbed on harder surfaces tend to differentiate into bone-like cells (Engler et al. 2006).

Cross-References

► Stem Cell

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Biological and Synthetic Membrane

► Bioartificial Synthetic Membrane

Biological Membrane

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Synonyms

Biomembrane

Introduction

Biological membranes are enclosing or separating membranes that act as selectively permeable barriers within living things. Biological membranes have dynamic structures composed of phospholipid molecules, proteins, and carbohydrates (Brown and London 1998; Diamond and Wright 1969; Lee 2003). Steroid cholesterol is also found in the biological membranes of eukaryotic organisms.

The phospholipid component of the biological membrane plays an important role in the property of biological membranes. A phospholipid layer consisted of a hydrophilic head that interacts with polar fluids (e.g., water), and its hydrophobic tail always meets with the hydrophobic tail of another layer (forming a phospholipid bilayer or a liposome) or its own (forming a micelle). This structure maintains the fluidity of cells and organelles. The embedded, integral, and peripheral proteins of biological membranes are used in communication and transportation of chemicals and ions. Typically, the phospholipid bilayer acts as an impermeable barrier to most molecules and molecules can only cross the membrane with the aid of proteins.

Biological membranes, in the form of cell membranes (i.e., plasma membranes), are selectively permeable to ions and organic molecules and thus could control the movement of substances in and out of cells. Cells also contain intracellular membranes, which act as the boundary of various intracellular organelles, e.g., the nucleus and the mitochondria.

Cross-References

- Bioartificial Synthetic Membrane
- Cellular Membranes

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Biological Membrane Reactors

- [Membrane Bioreactors](#)
- [Principle of Biocatalytic Membrane Reactors \(BMR\)](#)

Biomaterial

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A biomaterial is any material in contact with a biological system. The first nonbiological material entered in contact with the human body seem to date back to the prehistory 9000 years old with the “Kennewick Man,” who had a spearpoint embedded in his hip. This spearpoint was the first foreign material implant, which was “tolerated” by the body (Ratner et al. 2012). Although the use of biomaterials dates back to the ancient time, the study of biomaterials is about 60 years old.

Biomaterials can be classified on the basis of its (i) source in natural or synthetic materials if they are from nature or synthesized in laboratory, respectively; (ii) chemical nature in organic, inorganic, and composites; and (iii) degradation properties in biodegradable and nonbiodegradable. They can be used in biomedical devices for the replacement of an organ function or implanted into the body for the replacement of tissue, organ, or body parts. Biomaterials are also used every day in dental applications, surgery, and drug delivery (Williams 2009).

Natural-based polymers offer the advantage of being similar to extracellular matrix components, and they have binding sites for cells and adhesion molecules so that they usually avoid immunological reactions and toxicity. Their principal disadvantage lies in the development of reproducible production methods, because their structural complexity often makes modification and purification difficult. Additionally, significant batch-to-batch variations occur because of their “bio preparation” in living organism (plants, crustaceans) while their mechanical properties are also limited. Chemical modification and cross-linking are common methods for altering mechanical properties such as elasticity and tensile strength of natural materials which are often not appropriate for dynamic physiologic environments. The most frequently used natural biomaterials are the collagen derived from connective tissues of animals, fibrinogen obtained from plasma, and other proteins of ECM. Among natural biomaterials, polysaccharides are also frequently used. These natural polymers include agarose, hyaluronan, chitosan, and alginate. They are derived from plant (seaweed) or animal origin and are used as hydrogels to support wound healing and also cell growth and differentiation (Mano et al. 2007).

Synthetic biomaterials different from natural materials can be synthesized to give various properties and have high reproducibility, availability, lot-to-lot uniformity, and constant quality. They have a well-known structure and properties so that mechanical properties, degradation rate, shape, and composition can be adjusted to the specific application. However, the biocompatibility and immune reactions are the big concern because they often lack sites for cell adhesion therefore their interactions with cells could be questionable. Synthetic biomaterials include biodegradable polymers as poly(lactic-co-glycolic acid) (PLGA), poly-lactic acid (PLA), polycaprolactone (PCL), poly(ethylene glycol) (PEG), etc. and synthetic polymers (e.g., polyurethane, polyetheretherketone, polyethylene, polyvinylidene fluoride, polyvinyl alcohol, polymethyl methacrylate, polydioxanone, etc.). For example, PLGA is one of the most frequently used biomaterials applied in neural, bone, and

cartilage tissue engineering for its degradation rate that can be modulated. PLA is fast reabsorbed and widely used in tissue engineering applications alone or blended with other polymers. PCL is a very good elastic biodegradable polymer that finds several applications in tissue engineering. PEG that is used in pharmaceutical technology to modulate the degradation and absorption of bioactive proteins is also frequently used in bone, cartilage, nerve, liver, and vascular tissue engineering. Peptide-based biomaterials (e.g., the tripeptide Arg-Gly-Asp, RGD) consisting of short amino acid sequences exhibit cell-binding sequences found in the extracellular matrix natural proteins. Ceramic-based biomaterials that are totally or partly inorganic are applied in bone tissue engineering. Mostly they are shaped with heat-forming porous, brittle materials. Hydroxyapatite and tricalcium phosphate owing to their structural similarity to the mineral phase of bone are used alone or in combination with organic polymers like PLA, PLGA, collagen, or chitosan in the bone replacement or regeneration (De Bartolo and Bader 2013; Morelli et al. 2015). Metals like alumina and titanium alloys that are bioinert materials are used as implant materials where implants are subjected to extreme mechanical load, like articular prostheses, dental implants, or heart valves.

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Biomembrane

- Biological Membrane
- Cellular Membranes

Biomimetic Membrane Approach

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Biomimetic membrane approach is based on artificial membranes which imitate fundamental properties and functions of biological membranes. Biomimetics develops simple and efficient synthetic systems that mimic the formation, structure, or function of biological materials, leading to new, more efficient, and cheap applications. Major potential applications of biomimetic membranes are drug delivery, high-throughput screening, sensors, and separation and purification, possibly coupled with chemical synthesis (Hélix-Nielsen 2012). The same membrane can serve an opposite purpose and be used as an experimental model of biomembranes. The term biofunctional membrane is more appropriate for the membranes, which include biological components, such as specific enzymes, aquaporin, antigens, etc.

Biological membranes have a lot of different specific functions but all of them separate either two aqueous phases or an external gaseous and internal aqueous phase. Three major chemical components of biological membrane are proteins, lipids, and polysaccharides, and selective permeability is based on direct diffusion, facilitated transport with carriers, and penetration through the channels. Coupling with various energy sources, including light, adenosine triphosphate, and different ion concentrations separated by the membrane aqueous solutions, leads to the transmembrane active transport. Membrane processes can be controlled by temperature, transmembrane voltage, biochemical mediators, and drugs.

Amphiphilic molecules are usually able to spontaneously form liquid crystal structures.

These self-assembled structures, especially lipid monolayers, multilamellar vesicles, unilamellar liposomes, and bilayer lipid membranes can be used as models of biomembranes. To improve their stability, which is important for practical applications, lipid membranes are often immobilized on a solid support, which may be metal, glass, semiconductors, and polymers. The well-known example is Langmuir-Blodgett films. Lipids or their analogs may have an additional anchor group for tethering to a support. Sulfhydryl or disulfide groups are often used for tethering to the metals such as gold or silver, while methyl- and methoxy-substituted silane groups – for tethering to glass, quartz, silica, and mica. Micro- and nano-porous solid supports, including hydrophobic membrane filters, are also used to stabilize thin and nonstable bilayer lipid membranes.

Though the thickness of lipid membranes (~ 50 Å) and some other structural properties are similar to the characteristics of biological membranes, electrical conductivity and permeability for inorganic ions are often four orders of magnitude less than those of biomembranes with aqueous channels.

Nitrocellulose microfilters with pores filled with fatty acids and other lipid analogs are another type of stable biomimetic membrane (Kocherginsky and Lvovich 2010). These impregnated filters have nanolayers of water covering the internal pore surface and separating nitrocellulose and liquid crystal structures inside the pores. Aqueous nanolayers imitate aqueous channels in biomembrane and have cation/anion selectivity due to the presence of carboxylic groups immobilized on the nitrocellulose polymer chains. Electric resistance and many other physically independent properties of these membranes, including direct permeability of water, nonelectrolytes and respiratory gases (O_2 and CO_2), and other properties recalculated for 50 Å thickness, are very similar to parameters for biological membranes. Low molecular mass carriers can be dissolved in the impregnating oils, leading to imitation of secondary active transport of metal ions and even electrons, driven by transmembrane difference of pH. Kinetics may be

controlled by temperature-induced phase transitions and even membrane-active organic cations. The process may be used for water purification. Nitrocellulose-based biomimetic membranes may also be used in potentiometric drug sensors (sensitivity often is $10^{-5}M$), and combination with electrochemical tests makes this system attractive in the high-throughput drug screening, such as Parallel Artificial Membrane Permeability Assay (PAMPA).

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Biomimetic Membranes

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Biomimetic membrane is designed and fabricated by imitating the composition, structure, formation process, as well as functions of biological membrane. As we know, biological membrane is the vital structural basis in organism, on which the essential life activities in cell take place. The asymmetric and hierarchical bilayer structure formed by the in situ self-assembly of amphiphilic phospholipid and functional proteins (Nielsen 2009) ensures the biological membrane take important roles in keeping the environmental stability of cell, participating in the multiple interactions of different cells, and efficiently achieving the conversion of energies, the signal transduction between cells, as well as the conversion and transmembrane transport of some substances (Zhu et al. 2011). Biological membrane has a very sophisticated structure consisting of abundant

species of lipids and proteins, which is difficult to imitate completely due to the constraints of current science and technologies (Eeman and Deleu 2010). As a simplification and transition, biomimetic membranes containing part of (not all) the key components or characteristics of biological membrane are being actively developed in the last few decades.

Biomimetic membranes can be divided into two categories in terms of structural morphology: freestanding membrane and supported membrane. The freestanding membrane is often utilized for theoretical investigation purpose, in other words, as a simplified model for studying the structure and function of biological membranes. This type of biomimetic membranes mainly includes the lipid monolayer membrane and the bilayer lipid membrane or named black lipid membrane (BLM) (Eeman and Deleu 2010; Kim et al. 2012). The BLM is suitable for investigating membrane phase behavior and membrane processes such as membrane fusion and molecular recognition for its closer structure with biological membrane, while the lipid monolayer is suitable for mimicking and evaluating the insertion of amphipathic compounds (Eeman and Deleu 2010). The biomimetic membrane has provided an effective platform for exploring the complex structure and function of biological membrane, even though further endeavors both in biological science and fabrication technology are still needed.

The supported membrane often contains a bilayer residing onto a solid substrate, which delicately ameliorates the weak stability and short lifetime of BLM (Li et al. 2012). Furthermore, the self-assembly of block copolymer (block polymer membrane, BPM) as another approach to form the bilayer can be an alternative of BLM for its higher stability, controllability, and ability to prevent the direct contact of embedded proteins to solid substrate, which otherwise will inactivate the proteins (Duong et al. 2012; Nielsen 2009). The supported BLM or BPM can be prepared by several methods, of which vesicle collapse technique is commonly used (Eeman and Deleu

2010). In addition to act as model of biological membrane for investigating protein-lipid interaction, this type of biomimetic membrane performs well as functional membrane in various fields by incorporating different functional proteins: (1) energy conversion (energy converter, energy-production devices), (2) signal transduction (biosensor and bioanalysis), and (3) substance transport and conversion (drug delivery, immobilized enzyme catalysis, and membrane-based separation). To further exploit the application efficiency and area of biomimetic membrane, more efforts may be devoted to the following two aspects: (1) utilize channel proteins directly for the preparation of biomimetic membrane while acquiring the good control over the channel density and the protein activity and (2) deepen the insight into the structure-function relationship of membrane proteins.

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Biopolymers

- [Biodegradable Polymer for Membranes](#)

Bioreactor Membrane

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Synonyms

Membranes used for bioreactors

Introduction

A bioreactor membrane is a synthetic organic or inorganic membrane used for solid-liquid separation in membrane bioreactors (MBRs). The membranes can be pressure driven (microfiltration, ultrafiltration, nanofiltration, and so on) and osmotically (forward osmosis) or thermally driven (membrane distillation); however, pressure-driven membranes are currently more popular. In most cases, MBR refers to the combination of a membrane process with a suspended growth bioreactor that is applied for water/wastewater treatment and/or for other purposes (e.g., fermentation). When used in wastewater treatment, sound retention of suspended solids by bioreactor membranes enables the distinctive advantages of MBRs, including a reduced footprint, an independent control of sludge retention time and hydraulic retention time, a higher biomass concentration, and a high-quality effluent (Judd 2008; Wang et al. 2008; Meng et al. 2009).

Bioreactor membrane characteristics such as pore size, porosity, surface charge, roughness, and hydrophilicity/hydrophobicity have been proven to impact on MBR performance, especially on membrane fouling (Meng et al. 2009). A series of organic and inorganic membrane materials, including polyvinylidene fluoride, polyethylene, polyacrylonitrile, polyethersulfone, polytetrafluoroethylene, polypropylene, polysulfone, cellulose acetate, aliphatic polyamides, aluminum, zirconium, and

titanium oxide, have been used in bioreactors, and an ideal material should have low affinity with biopolymers/foulants, sound mechanical strength, and good separation efficiency and is nonbiodegradable and cost-effective (Su et al. 2014).

In recent years, dynamic membranes have been investigated in MBRs in order to improve membrane performance (Meng et al. 2009). Contrast to conventional synthetic bioreactor membranes, dynamic membranes can be formed by filtering a solution containing either inorganic or organic materials (particulate, colloidal, and even soluble substances) through a coarse support material (Fan and Huang 2002). The separation efficiency of dynamic membranes is comparable to microfiltration and ultrafiltration membranes once the dynamic membrane is well formed. There are two basic types of dynamic membranes: pre-coated and self-forming. The pre-coated membrane is produced by passing a solution of one or more specific components over the surface of a porous support. The self-forming membrane is formed by the components in the solution to be filtered (Meng et al. 2009).

Cross-References

► Ultrafiltration Membrane Bioreactor

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Biorecognition Substrate

► Biointerface

Biorefinery

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A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, heat, and value-added chemicals from biomass (NREL web site 2014). The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum (NREL web site 2014). Raw materials for biorefinery are renewable lignocellulosic biomass, which include agricultural residues, wood residues, food wastes, grass, sugarcane, algal biomass, etc. The products of biorefinery include various types of biochemicals (cellulose, hemicellulose, lignin, succinic acid, lactic acid, lipids, adipic acid, butanol, fatty alcohols and esters, ethyl acetate, glycols, etc.), biofuels (bioethanol, biogas, bio-oil), and electricity. There are three main technical pathways for biorefinery of lignocellulosic biomass: thermochemical conversion, physicochemical conversion, and biochemical conversion. Thermochemical conversion uses heat and catalysis to produce biofuels and bioproducts and includes combustion, gasification, pyrolysis, and liquefaction of biomass. Physicochemical conversion applies physical and chemical methods to produce biofuels and includes pressing/extraction and esterification. Biochemical conversion utilizes enzymes and/or microorganisms to convert lignocellulosic biomass into bioproducts and/or biofuels and includes hydrolysis and fermentation

and anaerobic digestion. A typical bioprocess for bioethanol production from lignocellulosic materials includes the following major steps: pretreatment, hydrolysis, fermentation, and product (bioethanol) purification (He et al. 2012). First, the lignocellulosic material is pretreated to remove lignin and hemicelluloses. The remaining cellulose is then hydrolyzed to produce sugars which are fermented to produce ethanol. Finally, the ethanol is recovered and purified for commercial application. Separation technologies play an important role in this biorefining process, including ion-exchange resins that have been used for the detoxification of fermentation hydrolyzates, distillation in the recovery of ethanol, and ethanol dehydration. Membrane separation has been utilized in various stages of this biorefining process, including concentration of bioethanol by using membrane bioreactors and the removal of water from ethanol solution (Abels et al. 2013). Basically, there are three generations of biofuels, based on the use of different lignocellulosic biomass. First-generation biofuels include bioalcohols, biodiesels, biogas, and biosyngas and are typically derived from sugar, starch, and vegetable oil (Demirbas 2011). Biofuels from agroforestry wastes including the stalks of wheat, corn, wood, and dedicated nonfood-based bioenergy feedstocks (e.g., *Miscanthus*, willow, and poplar) form the basis of the second-generation biofuels (Sims et al. 2010). Third (3rd)-generation biofuels are derived from algae (Costa and de Moraes 2011). The fast-growing rate and utilization of CO₂ as carbon source make microalgae a fascinating biomass for biodiesel production, due to the high lipid content in microalgae. Optimization of processes for effective and efficient biomass conversion for first-, second-, and third-generation biofuels and for true integration in a biorefinery will require appropriate separation technologies. Compared to other separation technologies, the low energy consumption, greater separation efficiency, reduced number of processing steps, and high quality of the final product are the main attractions of membrane

separation processes in biorefining and bioenergy production (de Morais Coutinho et al. 2009).

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Biorefinery with Membrane Operations

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Membrane separations have been widely used in various stages of biorefinery, including upstreams for product manufacturing and downstreams for product purification. Full-scale biorefinery with membrane operations includes wastewater biorefinery for bioenergy recovery using anaerobic membrane bioreactors (AnMBR), dehydration of bio-ethanol using membrane separations, and lignin separation in integrated forest biorefinery.

In wastewater biorefinery, the potential energy stored in the organic compounds can be recovered as bioenergy (methane or hydrogen) through anaerobic digestion. One successful example of

membrane technology in wastewater biorefinery is the development of AnMBR technology. AnMBR is an integration of membrane separation with anaerobic digestion technology for bioenergy recovery. The use of membrane completely retains the slow-growing methanogens and eliminates biomass separation problems. To reduce energy usage, biogas sparging is used for membrane fouling control. AnMBR has the advantages of small footprint, high productivity, superior effluent quality for water reuse, and system closure. AnMBR has been successfully used for food processing wastewater treatment (Christian et al. 2010) and alcohol stillage wastewater treatment (Grant et al. 2008) for bioenergy recovery in full-scale plants. This indicates the successful application of membrane technology in the production of first-generation biofuel (biogas). The AnMBR technology achieved a high chemical oxygen demand removal (>98 % and 99.4 %) and bioenergy recovery in food processing wastewater and distilled wastewater treatment.

In the production of bio-ethanol, the first- and second-generation of biofuel, membrane separation technology has been successfully applied to concentrate bio-ethanol from fermentation broth and replace distillation for dehydration of bio-ethanol to save energy. In bio-ethanol production, the membrane is incorporated with the fermenters to create a membrane bioreactor for biomass separation and bio-ethanol concentration (Abels et al. 2013). To produce high-purity bio-ethanol (>99.5 %), pervaporation has been successfully used for dehydration of bio-ethanol (Oliverio et al. 2010). The principle of membrane dehydration of bio-ethanol involves two steps: molecules diffuse through the membrane as permeate and vaporization of the permeate into vapor phase through vacuum. The membrane system can be directly integrated in the rectification of existing ethanol plants or new ethanol systems. In doing so the energy demand of the complete ethanol system is minimized by arranging an optimized equipment configuration and strict heat integration. Both polymeric and ceramic membranes are used for bio-ethanol dehydration.

Full-scale membrane dehydration plants have been in operations all over the world. Thirty-five to 70 % reduction in energy consumption was observed in the downstream of bio-ethanol production, as compared to the distillation processes (Oliverio et al. 2010).

In integrated forest biorefinery, membrane filter has been used for lignin recovery from black liquor in kraft pulp mills. The lignin recovery process includes CO₂ precipitation, lignin separation, acid washing, and product drying. In a pilot testing in lignin precipitation and filtration, a LAROX filter equipped with a filter cloth from Tamfelt (S-2108-L1) was used to separate lignin from the aqueous solution after coagulation (Kouisni and Paleologou 2010). A filtration rate of 50–60 kg/m².h was achieved with no black liquor pretreatment (oxidation). After pretreatment (oxidation) of black liquor, the filtration rate was increased to 150–180 kg/m².h (Kouisni and Paleologou 2010). A LignoBoost™ commercial lignin plant with a production capacity of 70 tons lignin/day has been in operation in Domtar in Plymouth, NC, USA, since 2013 (Mitchell 2013). Another new full-scale lignin plant using the LignoForce™ technology is being built in Alberta, Canada.

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Biorefractory Pollutants

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A variety of compounds are classified as refractory when they are poorly biodegraded and/or exhibit a low value for the ratio of biological oxygen demand to chemical oxygen demand (BOD/COD) (Frimmel et al. 2008; Kopinke et al. 2002). These compounds are resistant or difficult to biodegrade, are toxic or are inhibitory to bacterial growth, and present an increasing problem in water and wastewater treatment systems (Delay et al. 2015).

These compounds could be organic (halogenated organics, aromatic and aliphatic hydrocarbons, pesticides, pharmaceutical products) or inorganic (metals, nanoparticles). Their origin could be anthropogenic or natural.

Cross-References

- [Persistent Organic Pollutant](#)

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Biosensor-Based Membrane

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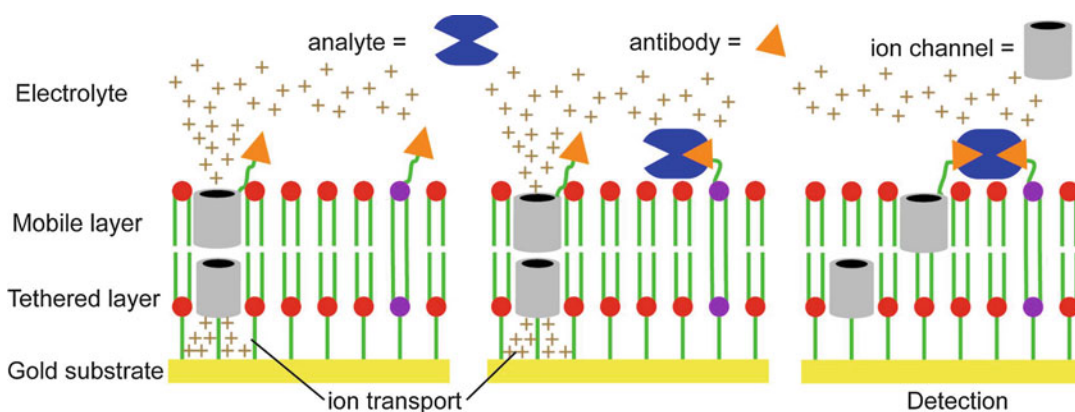
Synonyms

Membranes for biosensors

A biosensor is an analytical device used for the quantitative and qualitative detection of a specific analyte. A biosensor broadly consists of three main components: the biological sensing element which specifically interacts with the analyte, the transducer which is used to convert the signal from the bioelement-analyte interaction into a signal which is readable and reportable by the third component, the reading device (Fig. 1).

Membrane-based biosensors operate by reporting changes in ionic conduction through a

molecular membrane. These membranes consist of one or more lipid bilayer membranes, mimicking cell walls, upon a conducting (often gold) substrate (Cornell 2002). Many schemes have been reported for modulating the membrane ion conduction in response to the presence of a specific target analyte. The most common membrane-based biosensor was introduced by Cornell et al. where a mobile biological ion channel, initially gramicidin A, is tethered to an antibody of interest (Cornell et al. 1997). Under standard conditions, the ion channel is mobile throughout the membrane and predominantly exists in a dimer arrangement with a substrate-immobilized ion channel. Upon introduction of the target analyte, the analyte binds to both an immobilized antibody and the antibody tethered to the ion channel resulting in a conformational change of the ion channels, reducing conductance through the membrane (Cornell et al. 1997; Cornell 2002). From the change in conductance, a quantitative value of the amount of analyte present can be calculated. Membrane biosensors are promising for a range of diagnostic studies as the lipid membrane environment is ideal for the long-term storage of biological sensing elements (Oh et al. 2008).



Biosensor-Based Membrane, Fig. 1 Schematic of basic mechanism of a membrane-based biosensor based upon the change in conductance upon interaction between an antibody tethered to the ion channel and target analyte (antigen)

Cross-References

- [Cell Membrane](#)
- [Lipid Monolayer/Bilayer](#)

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Biosurfactant

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A biosurfactant (also called microbial surfactant) can be defined as a surfactant compound produced by microorganisms. Since surfactants are amphiphilic compounds, presenting both hydrophilic and hydrophobic moieties, they tend to move toward the interfaces, reducing the surface and/or interfacial tensions. These properties make surfactants excellent detergency, emulsifier, foaming, and dispersing agents (Mukherjee and Das 2010). Biosurfactants can be categorized mainly by their chemical composition and their microbial origin, being classified as glycolipids, lipopeptides and lipoproteins, phospholipids and fatty acids, polymeric surfactants, and particulate surfactants, and they are produced by a great variety of microorganisms, either secreted extracellularly or attached to parts of cells (Desai and Banat 1997). The biosurfactants have several advantages over chemically synthesized surfactants such as lower toxicity, higher biodegradability, and effectiveness at extreme temperatures or

pH values, besides presenting high surface activity and low critical micelle concentration values emerging as promising substitutes of the latter (Vaz et al. 2012).

Concerning the oil industry, biosurfactants can be used in the bioremediation of oil pollutants, in the enhanced oil recovery (reducing the capillary forces that retain the oil in the reservoir rock), in the treatment of oily sludges, and in the cleanup of storage tanks. They can also be applied in the pharmaceutical (due to their antimicrobial activity) and agricultural sectors (for the hydrophilization of heavy soil), as a pesticide, and in the food industry (Mukherjee and Das 2010; Banat 1995; Freire et al. 2009). They can also be used in the effluent treatment, for metal ion removal from aqueous solutions (Ramani et al. 2012) and to enhance the water/oil interaction in the degradation of high fat content effluents (Damasceno et al. 2012).

Regarding membrane separation processes, biosurfactants can be used in the micellar enhanced ultrafiltration, in which small contaminants, like heavy metal ions, are bound onto larger surfactant micelle complexes. These ions associated with surfactant macromolecules can be easily retained by an ultrafiltration membrane module. El Zeftawy and Mulligan (2011) investigated the use of rhamnolipid biosurfactants (glycolipids) in the micellar enhanced ultrafiltration of cadmium, copper, nickel, lead, and zinc ions with polysulfone hollow-fiber ultrafiltration membranes with molecular weight cutoff of 10,000 and 30,000. The authors reported nearly complete rejection of the ions, considering a feed concentration of 5 mg.L⁻¹, when using a rhamnolipid solution above its critical micelle concentration with both membranes. Even when increasing the metal ion content up to 50 mg.L⁻¹, the biosurfactant concentration could be adjusted to enable their complete rejection, with a permeate flux up to 200 L.h⁻¹.m⁻².bar⁻¹. Hong et al. (1998) also reported the ultrafiltration of copper, zinc, cadmium, and nickel ions using a polycarboxylic acid-type biosurfactant. The author used flat-sheet cellulose acetate membranes with molecular weight cutoff of 1,000 and 3,000, but the biosurfactant was not as

effective as the rhamnolipid reported by El Zeftawy and Mulligan (2011), leading to lower rejection values.

Another interesting application of biosurfactant was reported by Qin et al. (2012). These authors used rhamnolipid biosurfactants to enhance the frying oil degradation and to reduce the membrane fouling in a submerged membrane bioreactor, and an increase from 66 % up to 91 % in the oil removal efficiency was reported. The antifouling property of the biosurfactant was also confirmed.

Besides, the biosurfactants could be used to replace their chemically synthesized counterparts in several other membrane processes, like the micellar enhanced ultrafiltration of aromatic alcohols and in the emulsion liquid membranes, used to remove and/or purify metal ions, dyes, lignosulfonate, and lactic acid.

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Biosurfactant Production

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A biosurfactant can be defined as a surfactant compound produced by microorganisms. The biosurfactants have several advantages over chemically synthesized surfactants such as lower toxicity, higher biodegradability, and effectiveness at extreme temperatures or pH values, besides presenting high-surface activity and low-critical micelle concentration values emerging as promising substitutes of the latter (Vaz et al. 2012). In the present moment, the biosurfactants still present high production costs in comparison to the chemically synthesized surfactants. That is mainly the result of the low productivity of the microbial strains and the inefficient methodology of the bioprocessing. The technological improvement of the production process is essential (Kronemberger et al. 2008). In order to decrease the production costs, the scale-up of the whole production process, including upstream and downstream, should be developed.

One of the bottlenecks of the biosurfactant production relies on the fact that most of them are obtained through aerobic bioreactions. The use of the conventional submerged aeration can lead to the formation of very stable foams, causing serious operational problems. In order to

overcome that difficulty, a nondispersive oxygenation process using membrane contactors can be applied (Kronemberger et al. 2008, 2012; Gruber and Chmiel 1991). Kronemberger et al. (2008) investigated the rhamnolipid-type biosurfactant production in bioreactors with a nondispersive oxygenation device, obtaining productivities higher to the ones observed in shake flasks. This system was then successfully used in a fed-batch experiment, in order to assess the potential of a long-term production (Kronemberger et al. 2010). Coutte et al. (2010) reported a similar system for the production of lipopeptide biosurfactants, comparing internal and external nondispersive oxygenation.

Several authors have been investigating the recovery of biosurfactants, mainly surfactin, using ultrafiltration. Chen et al. (2008a) reported the flux decline in the ultrafiltration of surfactin using cellulose ester and polyethersulfone membranes with 100,000 Da of molecular weight cut-off, and the latter was recommended as the best one for this kind of experiment, even though the biosurfactant recovery was a little lower. Isa et al. (2007) investigated a two-step ultrafiltration recovery system for surfactin. In the first step ultrafiltration, surfactin was retained by polyethersulfone or regenerated cellulose membranes at above its critical micelle concentration. In the second step, with the same kind of membranes, after the disruption of the micelles by the addition of methanol, the purified surfactin was recovered in the permeate. Chen et al. (2008b) also reported the surfactin recovery, but using ammonium sulfate salting out, ultrafiltration, nanofiltration, and their hybrid process. The combination of salting out and ultrafiltration was selected due to the reduction of the fouling in the membranes used.

Another point of view should be the whole integrated production system supported by membrane processes. A system described by Coutte et al. (2013) comprises the nondispersive oxygenation of a bioreactor for the production of surfactin and the continuous cell removal and product separation using microfiltration and ultrafiltration modules, respectively. A pilot scale system, designed for the production of rhamnolipid-type

biosurfactants, with 200 L of useful volume was also described (Kronemberger et al. 2012). It comprises microfiltration modules for fresh medium sterilization, nondispersive oxygenation, another set of microfiltration modules with self-backwashing for cell retention, and a reverse osmosis unit used to concentrate the product and to recover the water as the permeate stream, enabling its reuse and minimizing the effluents.

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Biotechnology Processes Coupled with Membrane Separation

► Membrane Biotechnology

Biphasic Biocatalytic Membrane Reactors

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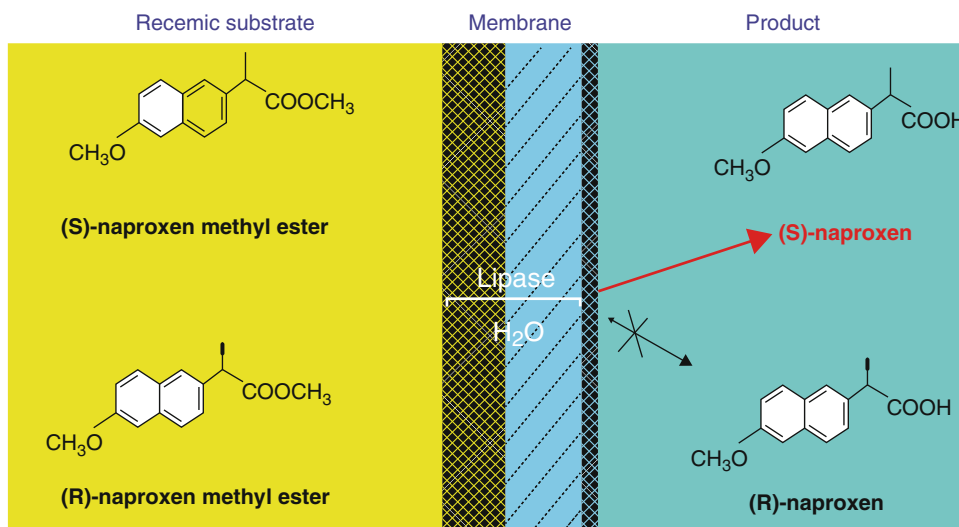
Synonyms

Multiphase enzyme membrane reactors; Two-separate phase biocatalytic membrane reactors

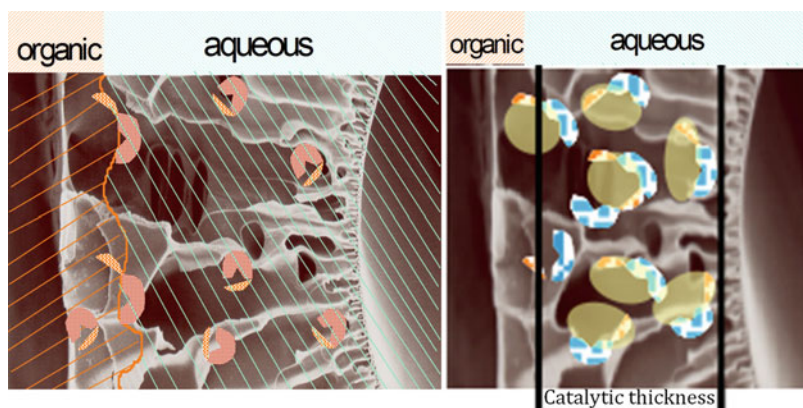
A schematic representation of a biphasic membrane is reported in Fig. 1. The system is suitable for bioconversions of low water soluble substrates. The enzyme loaded-membrane separates two immiscible phases: the substrate is present in the organic phase whilst the product is extracted in the aqueous phase. Particularly interesting is the

case where the biocatalyst is enantiospecific and converts only one of the substrate isomers giving in one step the production and separation of enantiomers in the optically pure form. The most studied enzyme in this systems are lipases. They are phase transfer catalysts activated by interface. When lipase is randomly loaded within the membrane and the two phases contact at a certain level of the porous thickness, only part of the lipase is located at the interface, whilst most of it is either in the water or in the organic phase (Fig. 2a). This results in an apparent lower activity of the immobilized enzyme.

An advanced development of multiphase reactor systems (emulsion enzyme membrane reactor) has been reported where the organic/water interface within the pores at the enzyme level is achieved by stable oil-in-water emulsion, prepared by membrane emulsification, so that each pore can work as a microreactor containing immobilized enzyme. In this way, the enzyme works in the membrane pores in the same conditions as in the stirred tank reactor, but with no shear stress due to stirring. Various configurations can be obtained. In one case the enzyme is immobilized within the porous matrix and the emulsion is fed to the membrane and pressed to pass through the enzyme-loaded membrane (Giorno et al. 2003). As long as the reaction rate



Biphasic Biocatalytic Membrane Reactors, Fig. 1 Biphasic membrane reactor for phase transfer catalysis



Biphasic Biocatalytic Membrane Reactors, Fig. 2
(a) Schematic representation of the organic/aqueous interface at a certain level within the porous membrane thickness, with lipase at the interface in the open conformation

(b) Schematic representation of the porous membrane thickness loaded with oil/water emulsion containing lipase at the interface. Here the catalytic thickness is much larger

Biphasic Biocatalytic Membrane Reactors, Table 1 Performance of enzyme in multiphase biocatalytic membrane reactor with different membrane materials

Membr. Type	Membr.cut-off (kDa)	Immobil. site	Immobil. enzyme (mg/cm ²)	(S)-naproxen production (mmol)	Enantio-excess (%)	Enantio-selectivity (—)
PA	10	Sponge layer	0.3	21	90	20
PA	10	Thin layer	0.08	6	35	2.2
PA	10	Thin layer	0.11	10	64	4.6
PA	50	Sponge layer	0.61	34	91	21
PA	50	Thin layer	0.19	3.5	91	21
PS	30	Sponge layer	1	38	81	10
PS	30	Thin layer	0.17	11	63	4.2
PP	0.2 m	Surface	0.14	21	94	25

balances the convective transport rate there is no significant influence of fouling. Emulsion enzyme membrane reactors can also be prepared by immobilizing the emulsion and the enzyme within the porous structure of the membrane thickness, so that to have a two separate phase enzyme-emulsion loaded membrane, as illustrated in Fig. 2b (Giorno et al. 2007). This latter configuration guarantees a high enantioselectivity of phase transfer catalysts activated by interface, thanks to the fact that all immobilized enzyme is located at the oil/water interface.

These configuration improved the selectivity and productivity of the biocatalytic system as well as its catalytic stability.

A comparison between performance of different membrane materials used in multiphase enzyme membrane reactors is reported in Table 1.

References

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Blending Modification of Membranes

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When using the word “blend,” we mean a mixture of two or more components with low or high molecular weight, organic or inorganic nature, and solid or liquid state. Physical or chemical blends with various degree of complexity can be produced depending on the nature of the mixed materials. Generally, in a blend we distinguish between a continuous film (*hosting matrix*) and a dispersed phase (*filler*) consisting of polymers, oligomers, nanoparticles, nanotubes, nanowires, zeolites, and so many others (Fig. 1).

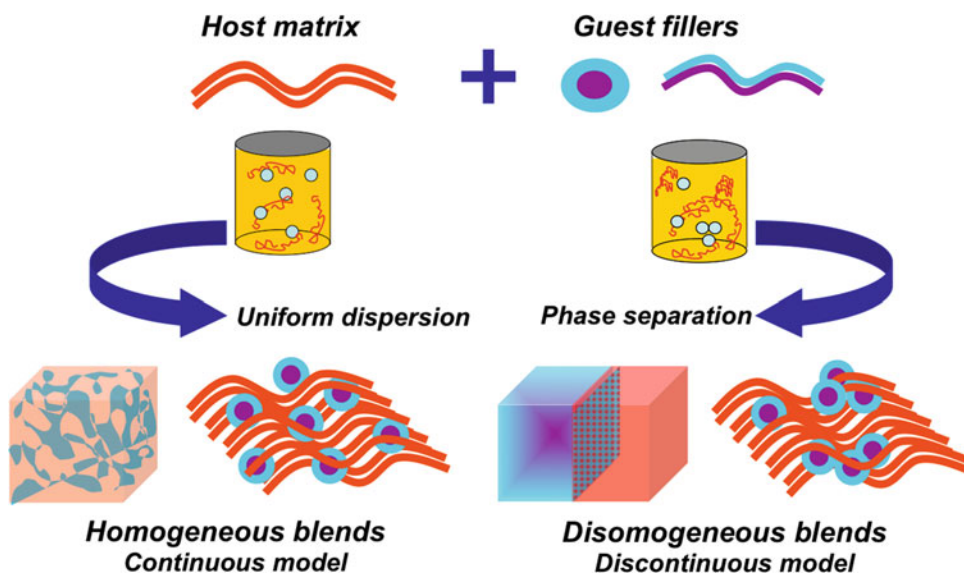
The blending is used for making new formulations with superior performance, when components with complementary functions are well interlaced and uniformly distributed. Major concerns are compatibility, uniformity, adhesion, and minimum loading for maximum surface area (Gugliuzza 2013; Gugliuzza et al. 2006). Segregation, nano-confinement, phase separation, and

discontinuity are frequent phenomena, which take place in solution or during fabrication of the composite (Gugliuzza et al. 2007; De Lorenzo et al. 2012). These events occur mainly when the mixed compounds do not exhibit compatibility and/or miscibility at all. In this respect, the glass transition temperature (T_g) could be a powerful tool for examining the degree of miscibility of binary blends, e.g., mixed polymers. When one T_g is obtained, the blend is considered fully miscible. If two T_g values are measured and a dependence on the composition is estimated, the blend is partially miscible. Finally, immiscible blends show distinct and independent T_g values, as illustrated by Fig. 2.

A set of equations can be useful to predict the x -dependence of T_g , where x is the composition. The Fox equation (1956) is the simplest one and is traditionally used for binary systems, thereby giving indication based on the properties of pure components:

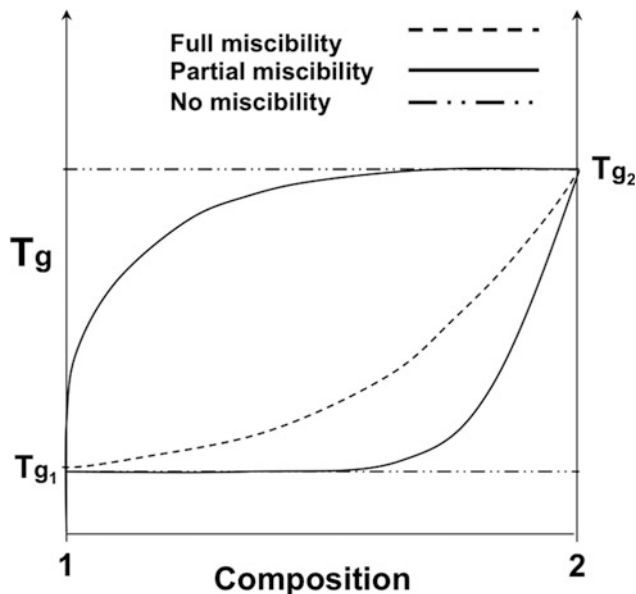
$$\frac{1}{T_g} = \frac{x_1}{T_{g1}} + \frac{x_2}{T_{g2}} \quad (1)$$

where T_g is related to the blend, whereas T_{gi} and x_i are glass transition temperature and composition of the i -esimo pure component, respectively.



Blending Modification of Membranes, Fig. 1 Examples of miscible and immiscible blends

Blending Modification of Membranes, Fig. 2 A schematic representation of the dependence of T_g on composition in binary polymer blends



The Gordon and Taylor equation (1952) includes an additional experimental parameter (k_{GT}) that considers unequal contributions of the components:

$$T_g = \frac{x_1 T_{g1} + k_{GT} x_2 T_{g2}}{x_1 + k_{GT} x_2} \quad (2)$$

Two other more complex relations are the Kwei (1984) and Brostow (2008), Eqs. 3 and 4, which take in account additional parameters such as K_{KW} , q , and a_i upon complexity of the polymer blend and/or copolymers:

$$T_g = \frac{x_1 T_{g1} + k_{KW} x_2 T_{g2}}{x_1 + k_{KW} x_2} q x_1 x_2 \quad (3)$$

$$T_g = x_1 T_{g1} + x_2 T_{g2} + x_1 x_2 \left[a_0 + a_1 (2x_1 - 1) + a_2 (2x_1 - 1)^2 + a_3 (2x_1 - 1)^3 \right] \quad (4)$$

In all equations the index 2 is referred to the component with the highest T_g , whereas x_2 is $1 - x_1$.

A good blend depends on the degree of interaction between the hosting matrix and the external surface area of the dispersed phase and can be

regarded as the result of the buoyancy of van der Waals forces and/or hydrogen bonds established at their interface (De Luca et al. 2009). Chemical functionalization and/or compatibilizing agents are two viable routes for strengthening these reciprocal interactions and dispersing the phases in continuous volumetric spaces. This needs to promote desired events in every region of the blend.

In membranes, the blend is a common practice to reinforce or produce specific properties, including transport, wetting, pores and mechanics, and so many others. Transport properties can be modified depending on the phase behavior and related morphology. Permeability, selectivity, or conductivity can be varied with respect to the upper bound relationship as a function of the orientation of the dispersed phase and/or the nature of the interface generated between the various components (Robeson 2010). Indeed, the molecular separation can be addressed via diffusion or sorption events dependently on free volume distribution and/or binding sites density.

Similarly, the blending can give new solutions to dry-wet membranes; changes in supramolecular chemistry can modulate the wettability, making the membrane usable for numerous times without damages and/or special treatments.

This approach is also preferred when pores must be generated through polymer networks. Pore-forming agents are often blended with polymers and, then, removed by washing treatments. This takes the advantage of generating empty spaces inside dense polymer networks, but the major difficulty is often the complete removal of the filler from the matrix. In this respect, a good compatibility between pore-forming agent and polymer matrix is necessary to produce a large number of uniform and regular pores through the network.

Finally, the blend is often preferred to provide composites with mechanical, chemical, and thermal properties beyond those observable for the single elements. Enhanced tensile properties along with reinforced resistance to high temperatures and harsh environments can be obtained by blending organic and inorganic materials in different ratios.

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Block Copolymer Membrane

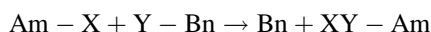
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Block Copolymers

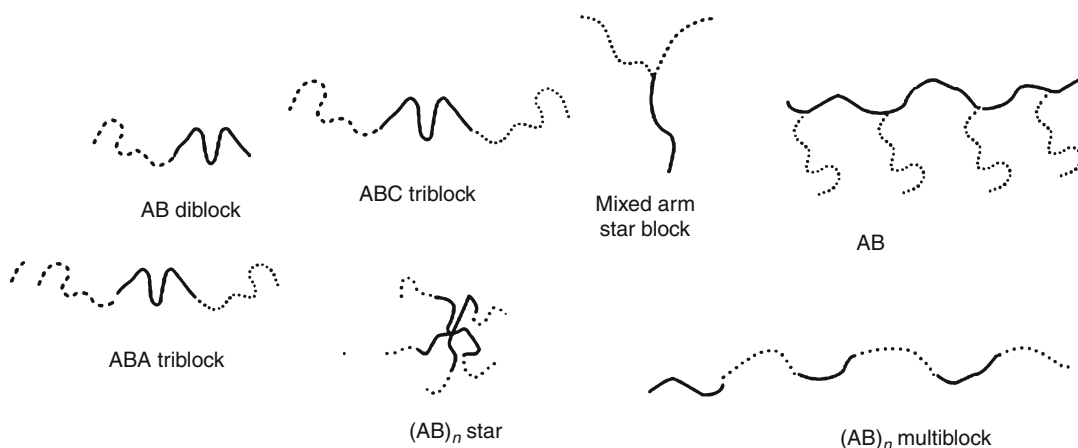
Block copolymers are polymeric materials in which macromolecules of two or more different homopolymers (blocks) are chemically bonded together to form complex macromolecules with linear (di-, tri-, multiblock copolymers) or nonlinear (mixed arm star, block, or graft copolymers) architecture (Fig. 1).

The routes of synthesis of block copolymers are two:

1. Creating centers or active sites (radical, anionic, cationic) of a polymer chain that can subsequently trigger the polymerization of a second monomer. If the location of the terminal active center is not specified, this definition also includes graft copolymers.
2. Condensation between functional groups located at the end of the polymer or prepolymer:



If the species are bifunctional, multiblock copolymers can be obtained. Despite the general indications just described, the interest for the production of block copolymers is focused on anionic initiators and polymerization processes having living character. This way, derived from the original studies of M. Szwarc (1956), provides

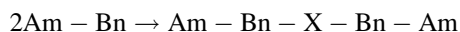


Block Copolymer Membrane, Fig. 1 Linear and nonlinear architecture of block copolymers

copolymer sequences well defined, with desired molecular weights, structures, and compositions. All this is achieved with diene monomers, vinyl (nonpolar), esters, ethers, or cyclic sulfides.

The key technologies for producing block copolymers with anionic initiators can be indicated schematically in the following way:

- Sequential polymerization of the monomers (especially in the case of di-blocks)
- Polymerization of the second monomer with the functionalized prepolymers of the first monomer
- Use of reactions of coupling between reactive terminals and a compound reagent that becomes the junction site:



- Use of bifunctional initiators

The synthesis of multiblock copolymers can be obtained by an alternately sequential addition of different comonomers into a living copolymerization system or, alternatively, by the coupling of difunctional homopolymeric precursors.

In the first case, anionic polymerization or, more recently, living radical polymerization methods can be in principle used. In real cases (Ekizoglou and Hadjichristidis 2002; Buzdugan et al. 2000; Reuter et al. 1991), each addition of a

new monomer will inevitably make some living chains dead because of impurities, leading to the resultant block copolymer with lower block numbers and broad molecular weight distribution. Therefore, the sequential addition method can only be used to make copolymers with a few blocks, such as triblock copolymers. Another limitation of the sequential addition of different comonomers is their reaction compatibility: each added monomer must be sufficiently reactive so that the chain can propagate. Often, a living A block can initiate comonomer B, but a living B block cannot initiate comonomer A.

In the second approach, multiblock copolymers could be in principle prepared by coupling (Yagci and Tasdelen 2006) different polymer chain di-ends terminated with suitable reactive groups or by linking (Yagci and Tasdelen 2006; Rahman et al. 2007) di-end-functionalized polymer chains using so-called difunctional linking agents in solution. However, both coupling and linking reactions are extremely ineffective when long polymer chains ($M_w > 5 \times 10^3$) are used as the precursors because most of the reactive end groups are segregated inside the polymer chains coiled in good solvent. Moreover, for long polymer chains, the concentration of the reactive end groups is too low to have an effective coupling or linking reaction because the overall polymer concentration cannot be too high. Therefore, the essential problem is how to expose and

concentrate the reactive end groups of long polymer chains, while the overall polymer concentration will not be increased.

Block Copolymers in Membranes

Copolymers, and in particular block copolymers (BCPs), in recent years have aroused great interest in the field of specialty polymer applications, including nanotechnologies (Park et al. 2003; Krausch and Magerle 2002; Hamley 2003; Lazzari and Lopez-Quintela 2003; Lu and Sastry 2007; Hawker and Russell 2005; Li et al. 2005; Segalman 2005; Cheng et al. 2006; Stoykovich and Nealey 2006; Krishnamoorthy et al. 2006; Li and Ober 2006; Fasolka and Mayes 2001; Darling 2007; Kim and Hinsberg 2008; Bates and Fredrickson 1999; Abetz and Simon 2005; van Zoelen and ten Brinke 2009), given their ability to self-organize into structures with periodicity down to the nanometer scale.

If the different polymer blocks are chemically incompatible, phase separation occurs with spontaneous segregation of different macromolecules in different microdomains (Fig. 2). Microdomains formed are not arranged in a random but show a regular arrangement which involves the formation of periodic structures.

This phenomenon, called “self-assembly,” determines the spontaneous formation of nanostructures. It is associated with the competition between the tendency to separation of phase, due to the incompatibility of the blocks, and chemical connectivity that prevents it; periodic

structures are formed in which the contact area between the incompatible microdomains is minimized. The minimization of the interfacial area between the domains involves a reduction in interfacial energy for which even if from an entropic point of view the individual polymer chains prefer a conformation random coil, in the case of block copolymers, macromolecules tend to assume more extended conformations at the interface between the two blocks so as to allow similar blocks to organize into microstructures that minimize the ratio (surface exposed/volume).

The frequency and size of these domains depend on the lengths of the regular blocks and, therefore, from the molecular masses.

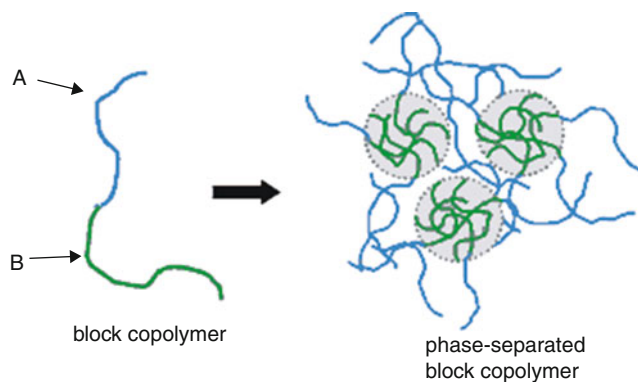
Block copolymers find many interesting applications in membrane technology.

Block copolymers have found application in a class of rubbery membranes, having the unique ability to separate CO₂ from gas streams, with a consequent increase in performance compared to that of the analogous homopolymers (Guan and De Simone 1994).

The polyethylene oxide [PEO] is, for example, one of the most interesting materials for the separation of CO₂, especially when cross-linked with other polymers or incorporated into block copolymers (Lin et al. 2006; Pethe et al. 2008). Because of its amorphous character and of its flexibility, it suitably directs the permselectivity of CO₂ through the polymer matrices, especially when the length of the segment, the weight, and the molecular ratio with the other blocks of the copolymer complexes are changed.

Block Copolymer Membrane,

Fig. 2 Schematic of “self-assembly” in BCPs due to phase separation



Bondar et al. (2000) observed that the permeability of CO₂ increases with the amount of polyether [PEO or PTMEO] when segmented block copolymers are incorporated into the polyether-*b*-polyamide, where they form the segregated phase of nylon-6 [PA6] or nylon-12 [PA12]. In particular, they have observed that the copolymers 57PEO/PA6 and 55PEO/PA12 exhibit a better selectivity to pure gas CO₂/N₂ 56 (PCO₂ 66 barrer) and CO₂/H₂ 9.8 (PCO₂ 20 barrer), respectively, compared to more conventional polymers rubbery and glassy.

Higher performance was observed when more than one unit polar (PEO and PA6) were included in the polymer chain, suggesting the critical role of interesting polar intermolecular interactions between the polymer chain and the penetrating molecules. Membranes PEO/PBT have been ad hoc designed in order to obtain block copolymers with high performance for the separation of CO₂ (Zhao et al. 2008). Separation factors for the pairs of gases, such as CO₂/H₂, CO₂/N₂, and CO₂/CH₄, were obtained in different ratios of the polymer chain. When mixed with the polyether glycol [PEG], a significant improvement of the permeability and selectivity for various block copolymers was observed.

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Blood Cell Origins

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Blood cell origins are from the hematopoietic stem cells (HSCs). HSCs can generate all types of the blood cells such as the erythrocytes (red blood cells), lymphocytes (T cells, B cells, and NK (natural killer) cells), monocytes, macrophages, neutrophils, basophils, eosinophils, megakaryocytes/platelets, and dendritic cells. HSCs are found in the bone marrow of adults, which includes the femurs, hip, ribs, sternum, and other bones. Cells can be obtained from the iliac crest part of the pelvic bone, using a special needle and a syringe; the cells removed are of two forms, i.e., as a smear and as a core biopsy. HSCs can be also found in the umbilical cord blood (UCB, 15–75/ml) and peripheral blood (1/ml). The low number of HSCs and small volume (50–150 ml) obtainable from a single donor of UCB limit direct transplantation of UCB to the treatment of pediatric patients. A density of 1.7×10^7 CD34⁺ cells (HSCs)/kg is necessary for the transplantation of UCB into patients (Higuchi et al. 2010). Therefore, UCB transplantation has been limited to children with an average weight of 20 kg. Numerous efforts have been made to expand HSCs ex vivo to improve

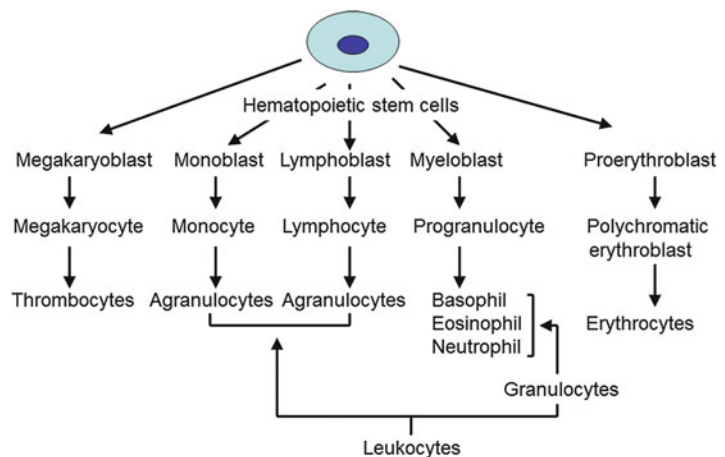
engraftment time and reduce the graft failure rate, particularly in developing this therapy for adult patients (Higuchi et al. 2010). HSCs cultured in 2D materials and in porous membranes can be possible to expand ex vivo.

Ex vivo expansion of HSCs is a hot topic due to the shortage of HSCs in clinical application. HSCs can be defined by surface marker of cells such as CD (cluster of differentiation). The cells of CD34⁺CD45[−] or CD34⁺CD38[−] are generally believed as HSCs, which are measured from flow cytometry where “+” indicates the expressing cells and “−” indicates non-expressing cells. CD133⁺CD34[−] cells are believed as more progenitor HSCs than CD34⁺CD38[−] cells.

Efficient cell separation is an important issue for the successful isolation and purification of HSCs. Centrifugation, affinity column chromatography, fluorescence-activated cell sorting (FACS), magnetic cell selection (MACS), and membrane filtration are techniques typically employed for cell separation (Higuchi et al. 2009). Highly purified cellular preparations are obtained using Ficoll–Paque method followed by FACS or MACS in conjunction with a fluorescently labeled antibody as the cell surface marker, while the cell separation by membrane filtration method is less specific, but is simple and easy operation, and sterility can maintain during the process. Only half an hour is necessary to purify HSCs from the blood by the membrane filtration method, while the conventional Ficoll–Paque followed by MACS method needs around 8 h (Higuchi et al. 2009) (Fig. 1).

Blood Cell Origins,

Fig. 1 HSCs are blood cell origins, which are multipotent stem cells giving rise to all of the blood cell types



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Blood Filtration

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Blood filtration is performed by hemodialysis membranes, leukocyte removal filter, and plasma separation membranes.

Blood is composed of plasma solution and blood cells. Several valuable proteins such as immunoglobulin, factor VIII, factor IX, albumin, vitronectin, etc. are contained in plasma solution. Blood cells are erythrocytes (RBC, red blood cells), lymphocytes (T cells, B cells, and NK (natural killer) cells), monocytes, macrophages, neutrophils, basophils, eosinophils, megakaryocytes/platelets and dendritic cells, and hematopoietic stem cells (HSCs). HSCs are found in the bone marrow of adults, which includes femurs, hip, ribs, sternum, and other bones.

In hemodialysis, the patient's blood is pumped through the blood compartment of a dialyzer, exposing it to a dialysis membrane. The dialyzer is composed of thousands of tiny synthetic hollow fibers. The fiber wall acts as the semipermeable membrane. Blood flows through the fibers, dialysis solution flows around the outside of the fibers, and water and wastes move between these two solutions. The cleansed blood is then returned via the circuit back to the body. Ultrafiltration occurs by increasing the hydrostatic pressure across the dialyzer membrane. This usually is

done by applying a negative pressure to the dialysate compartment of the dialyzer. This pressure gradient causes water and dissolved solutes to move from blood to dialysate and allows the removal of several liters of excess fluid during a typical 3- to 5-h treatment. Hemodialysis treatments are typically given in a dialysis center three times per week.

Hemodialysis membranes are typically prepared from cellulose materials or polysulfone-polyvinylpyrrolidone (PVP)-blended materials. Cellulose is hydrophilic and can be used as a hemocompatible material, whereas polysulfone is one of engineering plastics and needs to add a hydrophilic and hemocompatible material as a blending material. PVP shows relatively good hemocompatibility, and a more important fact is that PVP can be blended well with polysulfone. PVP is also used as a porogen in dialysis membranes of polysulfone. There is a recent demand for hemodialysis membranes that remove the low molecular weight proteins such as β_2 -myoglobin (MW 11500) and endotoxin (subunit of MW = 5,000–20,000), and useful albumin in the plasma should be recovered by the membranes. Polysulfone hollow fibers blended with PVP have been widely used as suitable hemodialysis membranes which satisfy this requirement (Higuchi et al. 2002).

Leukocyte removal filter: White blood cells (leukocytes) generate many adverse reactions during blood-transfusion therapy, which are graft-versus-host disease (GVHD), platelet refractoriness, nonhemolytic febrile transfusion reaction, and infection of viruses, such as human T-lymphotropic virus (HTLV), cytomegalovirus (CMV), and human immunodeficiency virus (HIV) (Higuchi 2010). It was found that most of the viruses infect specific type of leukocytes, such as granulocytes, monocytes, lymphocytes, B lymphocytes, T-helper cell ($CD4^+$ cell), and suppressor/cytotoxic T cells ($CD8^+$ cell) (Higuchi 2010). Therefore, removal of leukocytes in RBC and platelet concentrates as well as whole blood components is essential to prevent the adverse effect of contaminated leukocytes. Leukocytes can be removed using a filter comprised of nonwoven fabric or sponge materials as a filter

medium. The mechanism of leukocyte removal on the filters comprised of nonwoven fabric is based on the adsorption of leukocytes, while that comprised of sponge materials is based on the sieving effect and adsorption.

Plasma separation membrane: Plasma-exchange therapy has been increasingly applied clinically over the past few years. Membrane plasma separation has been used since 1979, which is similar to hemodialysis and hemofiltration. Plasma separation from whole blood is now performed routinely.

The materials of plasma separation membranes are typically made of nitrocellulose, polysulfone, and polypropylene.

Cross-References

- [Blood Cell Origins](#)
- [Blood Separation](#)
- [Blood Treatment Membrane](#)

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Blood Separation

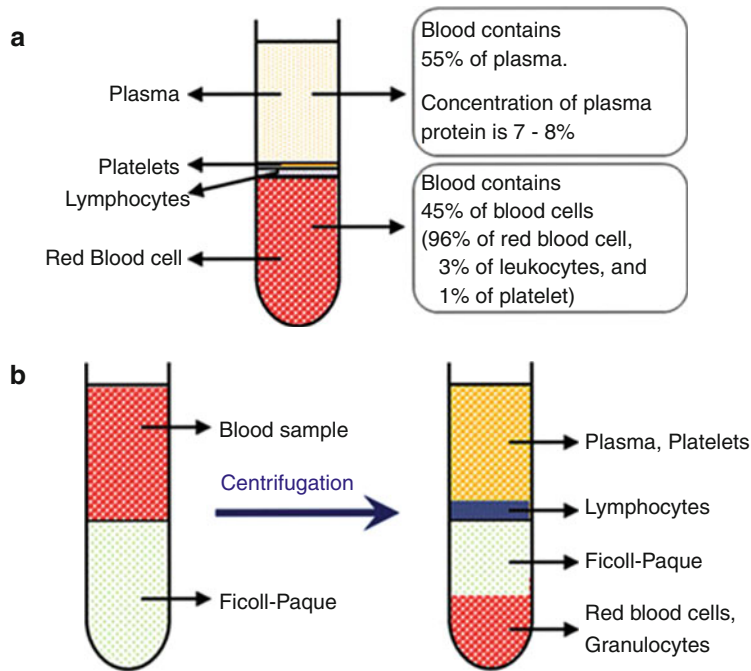
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Blood separation can be performed by centrifugation, magnetic cell selection system (MACS), fluorescence-activated cell sorting (FACS), and membrane filtration method. Blood is a living

tissue composed of several blood cells in plasma. The cellular elements of red blood cells (RBCs), platelets, and white blood cells make up 45 % of the volume of whole blood. Another 55 % is plasma, which contains 7–8 % of the plasma proteins and 92–93 % of water (Higuchi 2010). Figure 1 shows typical blood after centrifugation with and without addition of Ficoll-Paque (Ficoll-Hypaque) solution. After centrifugation of blood without addition of Ficoll-Paque (Ficoll-Hypaque) solution (native blood centrifugation), blood can be separated into plasma layer, platelet and leukocyte layer, and RBC layer (Fig. 1a). In this case, each layer contains other contaminant cells, e.g., RBC layer contains 96 % of RBCs, 3 % of leukocytes, and 1 % of platelets in blood cells. Platelets and leukocytes are also included in plasma layers. Platelet-rich plasma is necessary to use for the evaluation of biocompatibility of biomaterials (Higuchi et al. 2003). Platelet-rich plasma is obtained by centrifugation of peripheral blood or umbilical cord blood at 3,000 rpm. Platelet-poor plasma is used for plasma protein adsorption on biomaterials for the evaluation of biocompatibility of the biomaterials (Higuchi et al. 2003). Platelet-poor plasma is obtained by centrifugation of peripheral blood or umbilical cord blood at a relatively high speed of 3,000 rpm. Mononuclear cells including hematopoietic stem cells (HSCs) cannot easily be obtained by centrifugation of native blood. Therefore, Ficoll-Paque (or Ficoll-Hypaque) solution was injected into blood sample, and the mixed solution was centrifuged at $400\times g$ for 30–40 min at 20 °C (Fig. 1b). The upper layer contains plasma and platelets. Mononuclear cells including lymphocytes (T cells, B cells, and NK (natural killer) cells) and HSCs can be isolated from the upper second layer (Fig. 1b). When specific cells such as HSCs, T cells, N cells, or NK cells should be isolated, MACS or FACS are applied. Direct application of MACS and FACS to isolate the specific blood cells is difficult due to large quantity of RBCs in blood samples. After the mononuclear cells were isolated by Ficoll-Paque method, residual RBCs were removed by the treatment of lysing solution and then HSCs (CD34⁺ cells) can be isolated by MACS or FACS

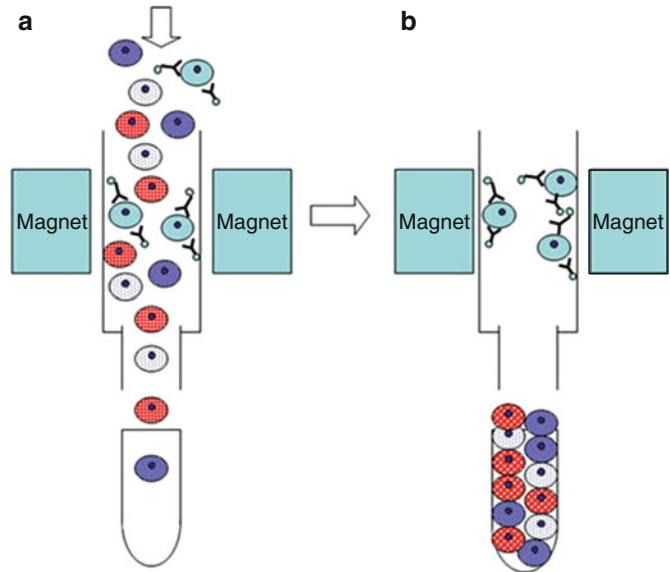
Blood Separation,

Fig. 1 Blood components after centrifugation of native blood (a) and before and after centrifugation of blood with Ficoll-Paque solution (b)



Blood Separation,

Fig. 2 Schematic mechanism of the separation method of cells by a magnetic cell selection system



treatment using antibody of CD34⁺ (Chen et al. 2012).

MACS is a sophisticated cell separation method, in which magnetic beads attaching a monoclonal antibody as the cell-surface marker are mixed with cells. Figure 2 shows the schematic mechanism of the separation method by an

MACS. The magnetic beads attaching the monoclonal antibody are separated by magnetic force to collect the specific marked cells. The MACS needs to use an expensive antibody conjugated with magnetic beads to bind to the target cells for the detection of the cells. Both cell separation methods using FACS and MACS are not

applicable if the antibodies to the specific markers on the surface of the target cells have not been established.

Blood cell separation through membrane filtration was recently reported by several researchers (Komai et al. 1998; Yasutake et al. 2001; Higuchi et al. 2004, 2008). Typical blood cell separation membranes are leukocyte removal filter (membrane) and HSC purification membranes.

HSC separation from peripheral blood and umbilical cord blood through surface-modified polyurethane membranes by membrane filtration method was reported (Higuchi et al. 2004, 2008, 2010). Peripheral blood or umbilical cord blood was permeated through the surface-modified membranes by filtration. HSCs are more adhesive cells than RBCs, platelets, and lymphocytes. Therefore, HSCs remained to adhere on the membranes during permeation of blood. The membrane-adhering HSCs were rinsed with phosphate buffer saline and subsequently human serum albumin or dextran solution as surfactant solution was permeated through the membranes. The HSCs can be harvested in the recovery solution of human serum albumin or dextran solution. The membrane filtration method of blood separation should be useful, because centrifugation instrument is not necessary to use and antibodies targeting specific cells are not used in the method, which cause contamination of antibodies in the blood cell samples.

Cross-References

- [Blood Cell Origins](#)
- [Blood Filtration](#)
- [Blood Treatment Membrane](#)

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Blood Treatment Membrane

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Blood treatment membrane is categorized as dialysis membrane, leucocyte removal filter, and plasma separation membrane.

Dialysis Membrane

Dialysis is a process for removing waste and excess water from the blood and is used primarily to provide an artificial replacement for lost kidney function in people with renal failure. Dialysis was used for those with an acute disturbance in kidney function (acute kidney injury), or progressive but chronically worsening kidney function.

Dialysis works on the principles of the diffusion of solutes and ultrafiltration of fluid across a semipermeable membrane. Blood flows by one side of a semipermeable membrane, and a special dialysis fluid flows by the opposite side. A semipermeable membrane (dialysis membrane, dialyzer) is a thin layer of material that contains the appropriate size of pores. Smaller solutes (urea, NaCl) and fluid pass through the membrane, but the membrane blocks the passage of larger substances such as red blood cells and large proteins (albumin, globulin). This is the filtering process taking place in the kidneys, when the blood enters the kidneys and the larger substances are separated from the smaller ones in the glomerulus (Daugirdas et al. 2006).

In hemodialysis, the patient's blood is pumped through the blood compartment of a dialyzer, exposing it to a dialysis membrane. The dialyzer is composed of thousands of tiny synthetic hollow fibers. The fiber wall acts as the semipermeable membrane. Blood flows through the fibers, dialysis solution flows around the outside of the fibers, and water and wastes move between these two solutions (Daugirdas et al. 2006). The cleansed blood is then returned via the circuit back to the body. Ultrafiltration occurs by increasing the hydrostatic pressure across the dialyzer membrane. This usually is done by applying a negative pressure to the dialysate compartment of the dialyzer. This pressure gradient causes water and dissolved solutes to move from blood to dialysate and allows the removal of several liters of excess fluid during a typical 3- to 5-h treatment. Hemodialysis treatments are typically given in a dialysis center three times per week (Daugirdas et al. 2006).

Hemodialysis membranes are typically prepared from cellulose materials or polysulfone-polyvinylpyrrolidone (PVP)-blended materials. Cellulose is hydrophilic and can be used as a hemocompatible material, whereas polysulfone is one of the engineering plastics and needs to add a hydrophilic and hemocompatible material as a blending material. PVP shows relatively good hemocompatibility and the more important fact is that PVP can be blended well with polysulfone. There are a lot of materials reported excellent

biocompatibility. However, these biocompatible materials cannot be used as blending materials in polysulfone dialysis membranes due to low mixing with polysulfone. PVP is also used as a porogen in dialysis membranes of polysulfone. There is a recent demand for hemodialysis membranes that remove the low-molecular-weight proteins such as β_2 -myoglobin (MW 11,500) and endotoxin (subunit of MW = 5,000–20,000) and useful albumin in the plasma should be recovered by the membranes. Polysulfone hollow fibers blended with PVP have been widely used as suitable hemodialysis membranes which satisfy this requirement (Higuchi et al. 2002).

Leukocyte Removal Filter

White blood cells (leukocytes) generate many adverse reactions during blood-transfusion therapy, which are graft-versus-host disease (GVHD), platelet refractoriness, nonhemolytic febrile transfusion reaction, and infection of viruses, such as human T-lymphotropic virus (HTLV), cytomegalovirus (CMV), and human immunodeficient virus (HIV) (Higuchi 2010). It was found that most of the viruses infect specific type of leukocytes, such as granulocytes, monocytes, lymphocytes, lymphocytes-B, T helper cell (CD4⁺ cell), and T-cell suppressor/cytotoxic cells (CD8⁺ cell). HTLV-1 and HIV mainly infect T helper cell, while CMV mainly infects granulocytes, monocytes, and lymphocytes. GVHD was mainly generated by T helper cell and T-cell suppressor/cytotoxic cells (CD8⁺ cell) (Higuchi 2010). Therefore, removal of leukocytes in RBC and platelet concentrates as well as whole blood component are essential to prevent the adverse effect of contaminated leukocytes. Leukocytes can be removed using a filter comprised of nonwoven fabric or sponge materials as a filter medium. The mechanism of leukocyte removal on the filters comprised of nonwoven fabric is based on the adsorption of leukocytes, while that comprised of sponge materials is based on the sieving effect and adsorption.

Filtration methods have several advantages compared to other methods of removing

leukocytes such as centrifugation. Virus contamination is lower in blood components during the process in the filtration method than in the centrifugation method due to mild operation and the ease of operation under sterilized conditions.

Leukocyte removal filters were typically made of polyurethane (PU) foaming membranes where the pore was made by salt leaching method and nonwoven fabric. The pore structure of both filters is found to be completely different, although the pore size of those filters was almost the same from capillary flow porometer measurements. The mechanism of leukocyte removal (i.e., separation of leukocyte from plasma and other blood cells) in leukocyte removal filters is based on leukocyte adsorption on the filters. The adsorption of leukocytes was affected significantly by filter materials, pore structure, and pore size.

Plasma Separation Membrane

Plasma-exchange therapy has been increasingly applied clinically over the past few years. Membrane plasma separation has been used since 1979, which is similar to hemodialysis and hemofiltration. Plasma separation from whole blood is now performed routinely. The materials of plasma separation membranes are typically made of nitrocellulose, polysulfone, and polypropylene.

Cross-References

- [Blood Cell Origins](#)
- [Blood Filtration](#)
- [Blood Separation](#)
- [Diafiltration](#)

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Blowdown Water

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Operational principle of steam and water boilers, cooling towers, evaporative coolers, and evaporative condensers is based upon the evaporation of water. Dehydration from these equipment leaves behind a solution enriched with nonvolatile substances mainly including salts of calcium, magnesium, sodium, and silica, requiring the discharge of contaminant-rich water. The drained volume of water in order to maintain an acceptable level of impurities in the evaporation equipment is known as blowdown water or bleed water or simply blowdown. In addition to the salts, blowdown water can also contain bacteria, algae, and pathogens. Increased concentration of minerals and other impurities is undesirable for several applications. For example, in steam boiler, the evaporation of pure water can lead toward the scale formation, water carryover with steam, and blockage of the piping system, while in case of cooling tower, concentrated blowdowns cause scaling and corrosion problems even in downstream equipment. The concentration of salts and other solid species in blowdown water is much higher than the original feedwater introduced.

In boiler, the blowdown water is discharged from the surface and bottom to get rid of floating and settled impurities, respectively. On one side, less amount of blowdown water may cause the

scale formation, water carryover, local heating leading toward the failure of boiler tubes, and less heat exchange rate, while the excessive discharge of blowdown water leads toward increased water usage, loss of energy associated with the discarded steam, large amount of makeup water, and excessive use of chemicals. Therefore, the quantity of blowdown water must be optimized.

Scarceness of freshwater, stringent environment regulations, and cost reduction are the driving forces for treatment of blowdown water. State-of-the-art treatment techniques for cooling tower blowdown water include lime-soda softening and thermal evaporation. The former removes hardness but involves the use of chemicals and produces sludge. Thermal evaporation, on the other hand, is highly energy intensive. Due to environmental concern, the concept of zero liquid discharge for treatment of blowdown water has gained popularity recently. The main tools to achieve zero liquid discharge under consideration include membrane filtration, electrodialysis, and evaporation.

In boilers, chemical pretreatment is applied to reduce the scaling problem and to enhance the heat transfer rate. These chemicals along with the other contaminants present into the boiler feedwater form sludge that settles down at the bottom of the boiler. Consequently, the blowdown becomes richer in impurities. Alternative membrane-based pretreatment can be applied to tackle these problems. For example, ultrafiltration has been used to affectively remove colloidal silica from the feedwater that imparts a vigorous effect in controlling the boiler blowdown (Kochi membrane systems, Inc. 2004). A more refined membrane process such as nanofiltration or reverse osmosis can further improve the consequence.

As far as the posttreatment of boiler blowdown is concerned, there have not been significant efforts devoted, probably due to high concentration and very complex nature of the waste stream. However, advanced membrane operations, especially membrane distillation, can be appropriate candidate due to high temperature and concentration of the stream and less fouling tendency of the MD process (Yu et al. 2013). In case of cooling tower, where the objective is to recover water with

quality equal or higher than that of makeup water, various membrane operations have been tested. Nanofiltration and reverse osmosis have shown the capability to treat the water to required purity level but usually require a pretreatment step. On the other hand, forward osmosis and membrane distillation have shown more interesting results in terms of less severe pretreatment requirements, operational stability, and less fouling problems.

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Blue Energy

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Introduction

The energy crisis is becoming one of the most pervasive problems facing the world today plagued with rapid economic growth and exponential increase in the global population. The key solution is sustainable energy that combines renewable energy with high energy efficiency to balance the growing energy needs without jeopardizing the earth's climate. Of great interest is the potential of

“blue energy” associated with osmotic power that can be harvested from the salinity gradient between two water streams such as seawater and freshwater, as seawater is globally distributed (Lewis et al. 2011), available all day and all year round. Two emerging membrane techniques, pressure retarded osmosis (PRO) and reverse electrodialysis (RED), are the primary methods proposed for recovering the osmotic energy.

PRO Working Principles

Three osmotic processes are illustrated in Fig. 1:

- Reverse osmosis (RO) that utilizes hydraulic pressure (ΔP) to overcome the osmotic pressure gradient ($\Delta\pi$) across a semipermeable membrane ($\Delta P > \Delta\pi$), leading to the net water movement from the concentrated feed (F) to the permeate (P) side.
- Pressure retarded osmosis (PRO) that applies a hydraulic pressure lower than the osmotic pressure gradient to the high-salinity stream (draw solution (DS)) ($\Delta P < \Delta\pi$), giving a net water flux in the direction toward the draw solution.
- Forward osmosis (FO) that uses the osmotic pressure gradient as the driving force without

hydraulic pressure ($\Delta P = 0$). Water flows from a less concentrated feed (F) to a more concentrated draw solution (DS).

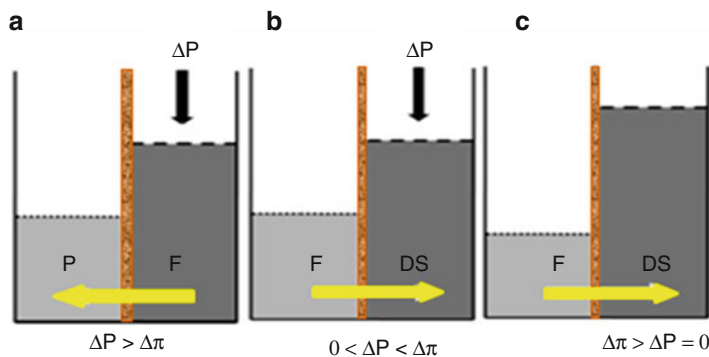
PRO is an intermediate osmotic process between RO and FO. As long as the osmotic pressure difference across the semipermeable membrane is greater than the applied pressure on a high-salinity stream, water will continuously flow from a low-salinity stream at a low pressure into the pressurized high-salinity stream. The increased volume of pressurized water is able to drive a turbine for power generation (Thorsen et al. 2009), resulting in the recovery of the chemical potential energy from the difference in osmotic pressures of the two water streams, as shown schematically in Fig. 2.

RED Working Principles

Unlike PRO, RED primarily depends on ion transport through the membranes when waters of different salinities are placed on opposite sides of either cation or anion exchange membranes. These membranes are stacked in an alternating pattern between a cathode (reduction electrode) and an anode (oxidation electrode) (Post et al. 2007). Another distinctive difference is that

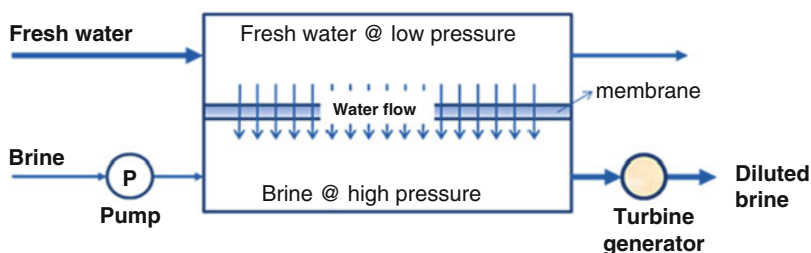
Blue Energy,

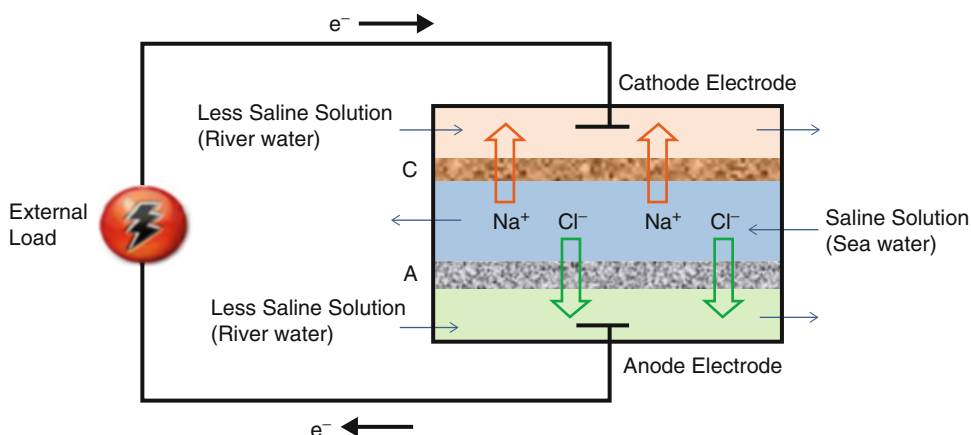
Fig. 1 Osmotic processes using semipermeable membranes: (a) RO; (b) PRO; (c) FO (arrow indicates the direction of water flow)



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Fig. 2 Schematic of PRO process for power generation





Blue Energy, Fig. 3 A simple RED process showing the transport of ions where *A* is an anion exchange membrane and *C* is a cation exchange membrane

the RED system is not pressurized like PRO to obtain the osmotic energy mechanically. Instead, direct electrical energy can be harvested from the movement of the electrons required to maintain electroneutrality of the overall solution as the ions from the saline solution are transported toward either the anode or cathode electrodes, as shown schematically in Fig. 3.

Specifically, electroneutrality is maintained via reduction at the cathode and oxidation at the anode via an external electric circuit that results in electrons being transferred from the anode to the cathode. Electrical energy can then be harnessed directly when an external load is connected to the circuit through the electrical current (movement of electrons) and the potential difference over the electrodes. Although the applied electrical potential difference will reduce the driving force of the ions when the external load is connected to the circuit, ions will continue to be transported toward the cathode and anode as long as the electrochemical potential difference is greater than the electrical potential difference.

Challenges and Potential Large-Scale Applications

The PRO process requires a robust membrane that can withstand high-operating pressures and achieve a reasonable high water flux (Chou

et al. 2012), while RED requires not only a membrane of minimal electrical resistance but also the whole stack design with a low electrical resistance. Normally, seawater and freshwater are used as a pair for both PRO (Lewis et al. 2011; Thorsen et al. 2009; Ramon et al. 2011) and RED (Ramon et al. 2011; Długołęcki et al. 2010) processes to harvest salinity gradient energy. Other salinity gradient pairs such as concentrated brine from seawater desalination (Enomoto et al. 2010) or hypersaline lakes such as the Dead Sea (Loeb 1976, 2001; Lacey 1980) are also possible resources for utilization. It is expected that large-scale applications for PRO and RED would be near river estuaries, hypersaline lakes, or seawater desalination plants. In particular, the co-location of PRO/RED with seawater desalination plants would allow the recovered energy from the RO brines to be used to desalinate the water.

In the oil and gas and mining industries, large amounts of water streams with high total dissolved salts (TDS) are produced from the hydraulic methods used in the harvesting of gas from coal beds (McBeth et al. 2003), oil from subsurface formation (Ahmadun et al. 2009), or from mining activities (Balaba and Smart 2012). Thus, the recovery of osmotic energy from such produced water streams is also possible for large-scale applications.

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Bore Liquid: Solvent and Nonsolvent

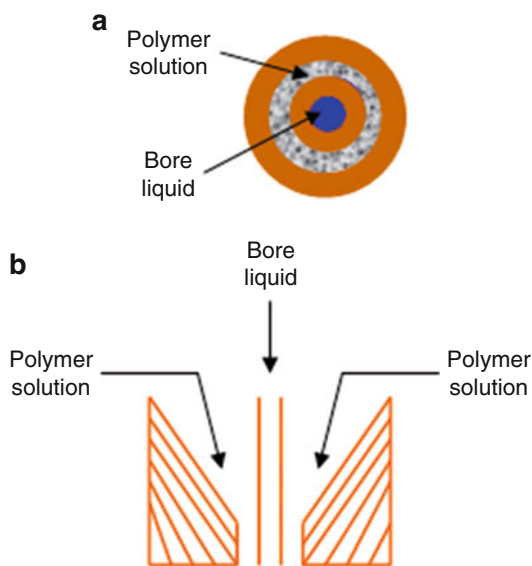
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B

Bore injection liquid is an internal coagulant pumped through the inner tube of the spinneret used for fabrication of hollow fibers by the dry/wet spinning technique or the wet spinning technique. Figure 1 shows schematic illustrations of the cross-sections of the spinneret used in these techniques. The spinneret has a tube-in-orifice structure with typical dimensions 0.5–1 mm inner diameter and 0.9–2 mm outer diameter.

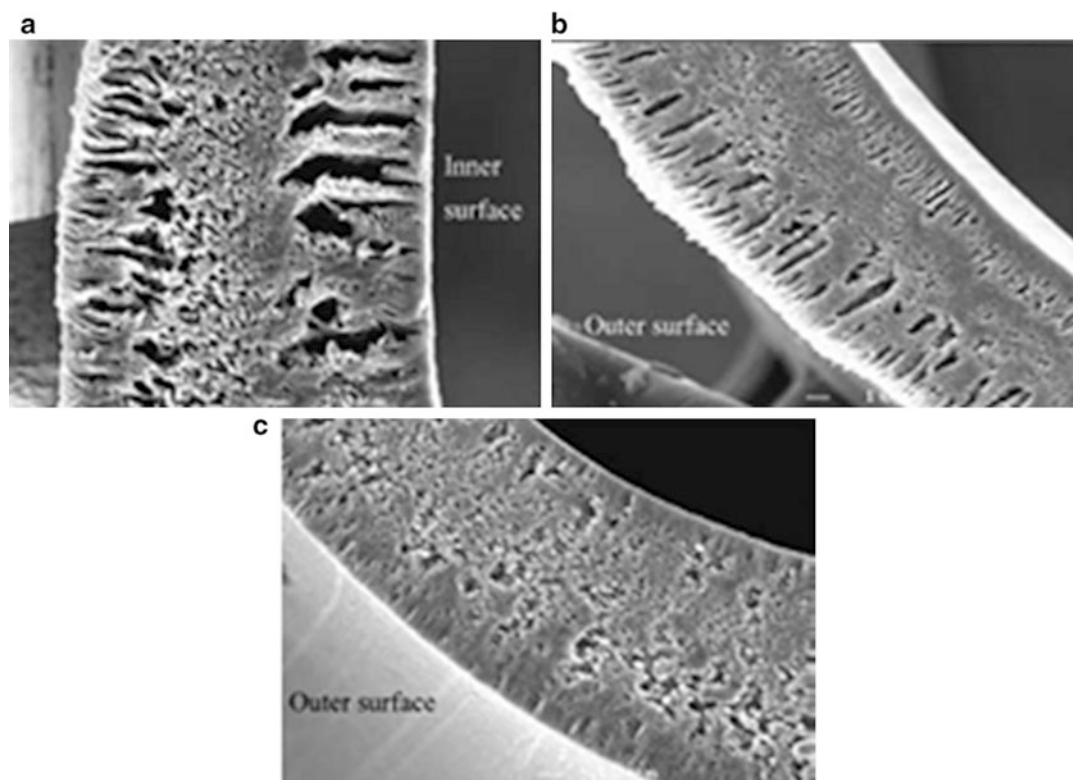
The bore liquid is one of the controlling parameters of the wet spinning and dry/wet spinning techniques used to fabricate hollow fibers. It must be a non-solvent or a non-solvent mixture exhibiting a low affinity with the polymer solution



Bore Liquid: Solvent and Nonsolvent, Fig. 1 Transversal (a) and lateral (b) cross-sections of a common spinneret used in dry/wet spinning and wet spinning techniques

(dope solution). The solubility parameter of the bore liquid must be different from that of the polymer to be coagulated. The interactions between solvent and coagulant and between solvent and polymer play important roles affecting the rate of polymer precipitation (coagulation, solidification). For poly(vinylidene fluoride) (PVDF) polymer solution as an example, water is a strong coagulant commonly used for fabrication of hollow fibers. In the dry/wet spinning or wet spinning, the polymer solution under gas pressure is extruded from the annular space of the spinneret, whereas the internal coagulant (bore liquid) is driven through the central tube of the spinneret either by gravity force or by means of a circulation pump. Coagulation of the internal surface of the nascent fiber starts immediately after its extrusion from the spinneret, whereas the external surface experiences coalescence, and orientation of polymer aggregates through the air gap before gelation in the external coagulation (i.e., non-solvent or non-solvent mixture) bath. The air gap is the vertical distance between the spinneret and the liquid coagulation bath and it may vary from 0 (wet spinning) to more than 1 m (dry/wet spinning). The bore liquid and the solvent exchange by diffusion and then the polymer solution become thermodynamically unstable. Demixing may take place from the bore side or lumen side and from the shell or outside of the as-spun fiber. Two types of demixing are possible: liquid–liquid demixing and gelation or crystallization. Gelation is not a phase separation process whereas crystallization involves a solid–liquid demixing. In order to determine the composition or temperature at which the solution is no longer thermodynamically stable, turbidity or cloud points must be determined. Cloud points are defined as the moment when the solution changes from clear to turbid. To localize the cloud point of a ternary system, a possible method is titration of polymer solution containing polymer and solvent with non-solvent or with a mixture of solvent and non-solvent at a given temperature until permanent turbidity is detected. The turbidity point can be detected by turbidity measurements or light scattering methods.

When a strong bore liquid coagulant such as water for PVDF polymer is used for the fabrication of a hollow fiber membrane, a dense and smooth surface with no obvious pores is formed. However, when a weaker coagulant is employed such as methanol, which may be mixed with water, the roughness of the internal surface of the formed hollow fiber may increase considerably due partially to the formation of pores. Figure 2 shows the effects of the bore liquid coagulant on the cross-sectional structure of porous hydrophobic hollow fibers prepared by the dry/wet spinning technique (Khayet et al. 2002). Water and 50 % (by volume) ethanol in water were used as internal and external coagulants. Different cross-sectional structures can be observed. In Fig. 2a prepared with water as internal and external coagulants, long finger-like voids are formed near the inner surface, while smaller cavities are formed near the outer surface. Between the inner and outer layers, sponge-like structure appears. The inner layer is reduced when ethanol is added to the internal coagulant as can be seen in Fig. 2b. A uniform sponge-like structure extends over the entire hollow fiber cross-section, in Fig. 2c, when ethanol is added to both the internal and external coagulants. The addition of ethanol delays the coagulation process, and a long finger-like structure changes to a short finger-like structure and further to a sponge-like structure. The slow coagulation of the hollow fibers can be explained on the basis of the mutual diffusivity of solvent/non-solvent exchange and solubility parameters of the materials involved in hollow fiber spinning. The addition of ethanol in water reduces the diffusion of non-solvent into the nascent hollow fiber and consequently decreases the rate of precipitation (coagulation, precipitation). The surface roughness increased when ethanol was added to the bore liquid coagulant, which is due to the increase of the pore size. The pores at the inner surfaces of the hollow fibers are larger than those at the outer surfaces, and the pore size increases both at the inner and at the outer surfaces as ethanol was added to the coagulants (Khayet et al. 2002). A decrease of the porosity of PVDF hollow fibers was also observed with the addition of ethanol in the bore liquid.



Bore Liquid: Solvent and Nonsolvent, Fig. 2 Cross-sectional scanning electron microscopy (SEM) structure of PVDF hollow fiber membranes prepared by wet/dry spinning technique with different coagulants: (a) water

coagulant, (b) internal coagulant 50 % ethanol in water and external coagulant water, (c) 50 % ethanol in water coagulant (Reprinted from Khayet et al. (2002), Copyright 2002, with kind permission from Elsevier)

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Boric Acid Separation by Membrane Contactor

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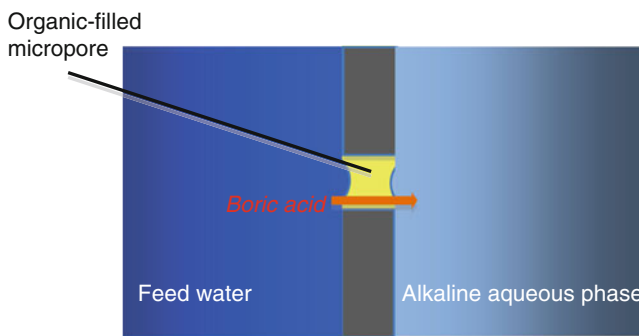
Boron is usually found in water as boric acid, and its concentration ranges from few ppb in river

water up to around 7 ppm in seawater and can be even higher in wastewaters discharged from some industrial plants. Due to its toxic effects on both humans and plants, the World Health Organization (WHO) has fixed at 0.3 ppm the maximum allowed concentration of boron in water. Different are the techniques that can be used for controlling the boric acid content of water, like adsorption, ion-exchange resins, solvent extraction, electrodialysis, multiple stages of reverse osmosis units (working at different pH), and membrane contactors. In particular, the effectiveness of membrane contactors has been confirmed using various configurations to treat waters containing boric acid.

Boric acid was selectively separated through supported liquid membranes containing inside micropores 1,3-diols (carrier) dissolved into o-dichlorobenzene. The membranes were

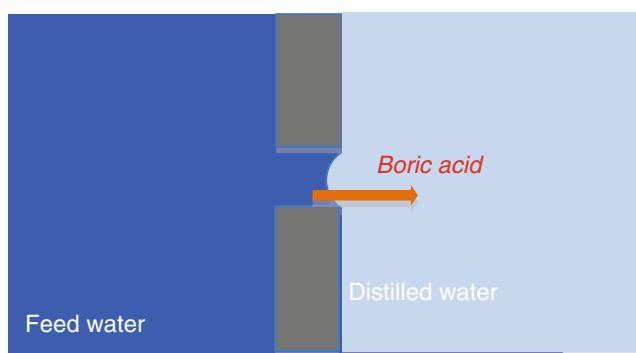
Boric Acid Separation by Membrane Contactor,

Fig. 1 Transport of boric acid through a supported liquid membrane



Boric Acid Separation by Membrane Contactor,

Fig. 2 Transport of boric acid in a hydrophilic membrane



hydrophobic and separated the aqueous stream containing boric acid from an alkaline aqueous phase, representing the so-called receiving phase; see Fig. 1 (Bachelier et al. 1996).

The removal of boric acid was also obtained by employing hydrophilic microporous membranes, sending distilled water as extractant phase. In this case, the membrane pores were filled with the aqueous feed, and, by properly acting on the pressures of the two phases, the interface was located at the membrane surface-extractant side, so that the boric acid removal occurred by simply diffusion from the feed to the extractant (Fig. 2). For practical implementations, an integrated membrane system where the extractant was continuously regenerated and recycled to the membrane contactor was also proposed and designed (Criscuoli et al. 2010a, b).

Successful performances of hydrophilic microporous membranes using distilled water as

extractant were also observed by Park and Lee (1995). Moreover, they found good efficiencies of anion exchange membrane contactors for the removal of boric acid from liquid radioactive wastes.

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Boron Reduction

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Synonyms

Boron removal

Characteristics

The boron element has an average concentration in the Earth's crust equal to about 10 mg/kg. Due to its strong affinity toward oxygen, it exists in nature mainly in the form of boric acids or borates. Boric acid and borates are mainly used in the glass and ceramic industry to obtain borosilicate glass, insulation fiberglass, flame retardant fiberglass, ceramic glazes, and porcelain enamels. Boron compounds are also used as a flame retardant in plastics and cellulosic insulation, neutron absorbers, herbicides (when at high concentrations) or fertilizers (when at low doses), and components of washing powders and soaps.

According to the WHO (2009) and (2011), average boron concentration in surface waters does not exceed the value of 0.5 mg/L. However, the amount of boron in these waters depends upon the presence of boron-bearing minerals in the proximity of water reservoirs. It may also be affected by the discharge of municipal and industrial effluents into the environment. On the other hand, naturally occurring boron is present in ground waters at a wide concentration range from <0.3 to >100 mg/L. This includes strongly mineralized, naturally carbonized geothermal waters. Considerable amounts of boron are also present in oceans, with an average concentration of 4.5 mg/L as reported by the WHO in 2009.

Despite the fact that boron is an important nutrient, it manifests toxic action against plants

and animals when found at high concentration in irrigation or drinking water. The effects of boron on plants and mammals were summarized by the WHO (2009), Kabay et al. (2010), and Hilal et al. (2011). Among the reported effects, the adverse impact of boron on the male reproductive system in rats, mice, and dogs was presented. Based on analysis of toxicokinetic of boron, the WHO proposed a guideline value for boron in drinking water of 2.4 mg/L in 2011. In areas with high natural boron levels, local regulatory and health authorities are, however, advised to consider values in excess of 2.4 mg/L by assessing exposure from other sources (e.g., food).

The low drinking water boron content limit implies the necessity for a reduction of boron content in drinking water, especially when seawater or boron-rich underground waters (e.g., geothermal waters) are to be treated. There could also be a need for boron removal from industrial and municipal effluents that contain more than the WHO guideline value. Conventional methods for water treatment do not significantly remove boron. The methods proven to be efficient in a reduction of boron content in waters are either adsorption or membrane based. Adsorption-based methods for boron removal include coagulation with metal hydroxides, adsorption on clays, fly ashes, and activated carbon (WHO 2009). Also, successful boron reduction with conventional anion exchange resins or resins functionalized with N-methyl D-glucamine (Chillon Arias et al. 2011) was reported. Among the membrane-based methods, boron removal by reverse osmosis is reported most commonly. Also some achievements in boron removal with ion-exchange membranes as well as boron removal by electrodialysis are presented. In addition, some hybrid systems, which combine membrane filtration with sorption, are proposed, e.g., the adsorption-membrane filtration (AMF) system. In this system, microparticulate boron selective resin suspension is recirculated in the retentate. Boron species remains adsorbed on the resin, while the boron-depleted water is continuously separated by microfiltration. According to

Kabay et al. 2008, the main advantage of the AMF over other methods of boron separation lies in the fast removal of boron, ease of sorbent separation, and low operating pressure.

According to the WHO (2009), the abovementioned methods for boron removal are likely to be prohibitively expensive, and blending with waters of low boron content may be the only economically feasible option to reduce high concentrations of boron in water.

Cross-References

- [Boron Removal by Electrodialysis](#)
- [Boron Removal by Reverse Osmosis](#)
- [Boron Removal with Ion-Exchange Membranes](#)

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Boron Removal by Electrodialysis

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As in the case of boron removal by reverse osmosis, the effectiveness of boron removal by electrodialysis (ED) is strongly affected by the aqueous chemistry of the boron species. In aqueous solutions, boric acid may exist in the form of boric acid, metaborate, and polyborates. Boric acid as a weak electrolyte ($pK_a = 9.2$) dominates in diluted aqueous solutions of a pH equal to or less than 9, while at higher pH borate ions dominate. Therefore, the effectiveness of boron transport across ion-exchange membranes (IEM) in the electrodialysis process needs to be discussed with regard to the type of the species that dominates in the dilute.

The Effectiveness of Boric Acid Transport in ED

Boric acid, H_3BO_3 , is a small and electrically neutral species. The reported boric acid removal efficiencies and electric current efficiencies in ED are poor when compared to ionic species (Melnik et al. 1999; Turek et al. 2005, 2007, 2008a; Kabay et al. 2008; Banasiak and Schafer 2009; WHO 2009). In fact, boric acid fluxes across IEMs are so low that the possibility of boric acid separation from ionic species, strong acids (Melnik et al. 2005, 2007) and salts (Turek et al. 2005, 2007; Bandura-Zalska et al. 2009; Dydo 2012a), by the use of electrodialysis is considered. Employing this method, ionic species are effectively transported across IEMs while boric acid remains in the ion-depleted dilute solution.

The type of the membrane, the dilute boron concentration, the presence of ions in the dilute, and the electric current density were shown to affect the rate of boric acid transport across IEM to a great extent (Melnik et al. 1999; Yazicigil and Oztekin 2006; Kabay et al. 2008; Dydo 2012a).

Boron Removal

- [Boron Reduction](#)

The reported mechanism for boric acid transport across IEMs is diffusion (Dydo 2012b); however, the flux of boric acid was found to increase with an increase in the flux of ionic species. This was suggested to be the result of a kind of ion-coupled transport of boric acid across IEMs. The effectiveness of such a transport was found to decrease in the following ion series: sulfate $\gg$ nitrate $\gg$ chloride. It was also reported that most of the boric acid was transported across anion-exchange membrane (AEM).

Turek et al. (2008b) reported high boron fluxes and exceptionally high electric current efficiencies of up to 220 % when boric acid was transported from ion-depleted, neutral or acidic, dilute into the alkaline concentrate of pH >11. Such a behavior was identified to be the result of Donnan dialysis, in which hydroxyl acts as a carrier for boric acid. However, in the light of recent reports, simple boric acid diffusion should explain the results as well.

Tentative results on boron removal by electrodialysis units equipped with ion-exchange spacers were also presented by Oren et al. in 2006. The possibility of up to an 80 % reduction of boron from water containing 4.5 mg/L was reported.

The Effectiveness of Borate Transport in ED

Melnik et al. (1999), Yazicigil et al. (2006), and Kabay et al. (2008) reported that as the pH of boron-containing water was brought up to just above the value of 9, a significant increase in the rate of boron transport across IEMs is observed. Moreover, Melnik et al. (1999) reported that in the case of heterogeneous membranes, an increase in the boron transport rate across anion-exchange membrane at pH >9 is accompanied by a decrease in the rate of boron transport across cation-exchange membrane (CEM). It is clear that under these conditions (pH >9), borates are the boron species that dominates and their transport across AEMs rather than CEMs should be discussed. The effectiveness of borate transport across AEMs in ED systems was found to depend

upon the pH of the dilute, the type of the membrane, dilute boron concentration, and the kind of the ion cotransported across the membrane. Yazicigil et al. in 2006 reported that at a dilute pH of approx. 9, there is a maximum boron transport rate, and at higher pH the rate of boron transport decreases. These results are contradictory to those presented by Melnik et al. (1999) (heterogeneous membranes), Turek et al. (2007), and Kabay et al. (2008), according to which there is a continuous increase in the rate of boron transport with dilute pH even when above 9.0. However, the Yazicigil et al. (2006) results seem to be justified by high boron concentration (0.1 mol/L) in their experiments. Similar behavior was observed by Ayyildiz and Kara in 2005. It is agreed that an increase in dilute boron concentration causes an increase in boron (borate) flux (Yazicigil et al. 2006; Kabay et al. 2008; Turek et al. 2008a). It is also agreed that boron (borate) is transported faster in the presence of chloride ions than in the presence of sulfates (Yazicigil et al. 2006; Kabay et al. 2008) or nitrates.

In 2005 and 2008a, Turek et al. analyzed the effect of salinity on the electric current efficiency of boron (borate) transport. They found that the observed electric current efficiencies are low as long as dilute salinity remains high. During the initial part of the experiments, no, or almost no, boron was transported from the dilute. Then, i.e., when more than 90 % of the Cl^- was removed from the dilute, a dramatic increase in boron (borate) electric current efficiency was observed. This increase was accompanied by an increase in boron flux. Such an effect can be identified as the result of low borate mobility (diffusivity) when compared to other ions present in the waters, i.e., Cl^- . As long as there are ions of higher mobility than borates in the dilute, boron (borate) flux remains low. However, even in an ion-depleted dilute, the electric current efficiency of boron (borate) transport has not exceeded the value of 30 %. The remaining percentage of the electric current was probably utilized for hydroxyl ion transport. A considerable drop in the pH of the dilute was reported afterwards. This resulted in a drop in dilute pH and in a consequent reduction in

the flux of boron since all the borate present was converted into boric acid. So the low electric current efficiency of borate transport in an ED system and the necessity for deep dilute demineralization make the economic feasibility of borate removal by ED questionable.

Cross-References

- [Boron Reduction](#)
- [Boron Removal by Electrodialysis](#)
- [Boron Removal by Reverse Osmosis](#)

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Boron Removal by Reverse Osmosis

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Reverse osmosis (RO) is a commonly applied membrane technique of desalination capable of producing permeates of drinking-water quality. In most cases, the boron content in the product should not exceed the WHO 2009 and 2011 guideline value of 2.4 mg/L. The effectiveness of boron rejection by reverse osmosis membranes is, however, strongly affected by its concentration in the feedwater and the aqueous chemistry of boron specie (Kabay et al. 2010; Hilal et al. 2011). In aqueous solutions, boric acid may exist in the form of boric acid, metaborates, and polyborates. Boric acid as a weak electrolyte ($pK_a = 9.2$) dominates in diluted aqueous solutions of a pH less than 9. Since the pH of most naturally occurring waters is lower than 9, the rate of boric acid transport determines the effectiveness of boron removal by RO.

According to Kabay et al. 2010, the rejection of boric acid by RO membranes is, however, low due to its small size and lack of electric charge. The reported boron rejection coefficients range from around 20 % in the case of old RO membranes to approx. 90 % in the case of modern RO

membranes (WHO 2009; Kabay et al. 2010; Hilal et al. 2011).

The effectiveness of boron removal from seawater by RO can be enhanced by adjusting the feedwater pH to above the value of 9.25. The monoborate anion, which dominates in diluted solutions at $\text{pH} > 9.5$, was found to be rejected more effectively than boric acid due to its larger size and discrete charge (Kabay et al. 2010; Hilal et al. 2011). The reported boron rejection coefficients at $\text{pH} = 11$ exceeds 99 % in the case of dense seawater reverse osmosis membranes. Also, in the case of boron-rich geothermal waters and industrial wastewaters, high boron rejection is observed only at $\text{pH} > 10.5$ (Koseoglu et al. 2010; Dydo et al. 2005). Furthermore, it was shown that the effectiveness of boron removal can be further enhanced by creating borate complexes (esters) with polyhydroxyl alcohols (Geffen et al. 2006; Dydo et al. 2012), although again, under alkaline conditions only.

The results of mechanistic studies on boron rejection by reverse osmosis membranes conducted by Sagiv and Semiat (2004), Hyung and Kim (2006), Hun et al. (2009), and Tu et al. (2010) showed that permeabilities of boric acid are at least one order of magnitude larger than those of monoborate ion. It proves more intensive diffusion of boric acid than of borate across RO membranes. Also, the reflection coefficients for boric acid (<0.985) are considerably lower than those specific for monoborate (>0.995) as reported by Hyung and Kim (2006). This, in turn, indicates strong boric acid–water interaction.

Feedwater pH is said to have a dominant impact on boron rejection by RO membranes (Hilal et al. 2011). Among other RO parameters that affect boron rejection are: operating pressure (increase), feed temperature (decrease), feedwater salinity (decrease), and recovery (decrease).

However, RO systems cannot be directly operated at high feedwater pH due to the possibility of membrane scaling with insoluble calcium and magnesium basic compounds. Therefore, several modifications to the operation of RO and its design have been proposed. In general, a cascade design for RO systems in which a fraction of the first stage permeate is treated in the following RO

stages (if possible at elevated pH's) and a blending of all the permeates produces water of the desired quality (Hilal et al. 2011; Faigon and Hefer 2008). This design was successfully applied, e.g., in the full-scale seawater treatment plant in Eliat.

Cross-References

- Boron Reduction
- Boron Removal by Electrodialysis
- Boron Removal with Ion-Exchange Membranes

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Boron Removal with Ion-Exchange Membranes

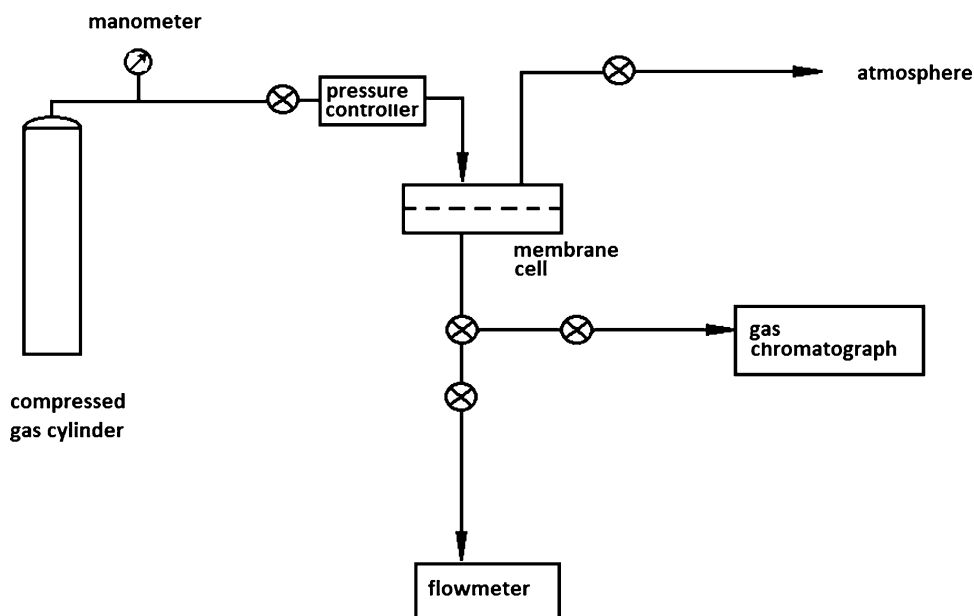
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Apart from boron removal by electrodialysis, ion-exchange membranes are able to transport boron in the so-called Donnan dialysis (DD) or diffusion dialysis processes (Fig. 1).

Ayyildiz and Kara (2005) examined the effectiveness of boron transport across anion-exchange membranes in a DD process. They found that boron flux depends upon the membrane, concentration of boron in the feed solution, pH of the feed and receiving solution, presence of the

accompanying ions in the feed solution, and the type of the carrier anion in the receiving solutions. The effect of pH of the feed solution was found to be complex. At high boron concentration (0.1 mol/L), maximum boron flux was observed at around the pH of 9.5, while in the case of a diluted solution (0.001 mol/L), maximum boron flux was observed at the maximum examined feedwater pH of 11.5. Such behavior was explained by the formation of polyborate ions at high boron concentrations and their absence in diluted solutions. The maximum rate of boron transport at the pH of around 9.5 in the case of concentrated boron solution was later confirmed by Yazicigil et al. in 2006. Ayyildiz and Kara in 2005 reported also that the pH of the receiving phase affects boron flux with its maximum at around a pH of 9.5. Moreover, the boron-accompanying anions, chlorides, bicarbonates, and sulfates, were found to affect the rate of boron transport in DD with a maximum observed in the presence of bicarbonate. On the other hand, the highest boron transport rates were observed with sodium chloride in the receiving solution. Neosepta AHA and AMH membranes produced similar fluxes of boron, while the superiority of



Boron Removal with Ion-Exchange Membranes, Fig. 1 Boron Removal with Ion-Exchange Membranes

AFN was clearly seen. In 2011, Kir et al. showed that plasma modification of the existing anion-exchange membranes may result in a significant enhancement of the rate of boron transport in a DD process.

The mechanistic study on boric acid transport across cation-exchange membranes (CEMs) in a DD process was presented by Goli et al. in 2010. It was reported that the membrane diffusion coefficients for boric acid depend not only upon the manufacturer of the CEM but also upon the type of the cation present in the membrane. The same behavior is reported for arsenite. In general, in the presence of monovalent cations in the membrane, higher fluxes of boron were observed than in the presence of divalent cations. Such a behavior was later confirmed by Dydo in 2012. The existing differences in boric acid membrane diffusion coefficients were rationalized by Goli et al. (2010) as being the result of the change in the mean viscosity of the solution confined in membrane pores.

In 2007, Bryjak et al. proposed a Donnan dialysis-based method for the regeneration of finely divided boron selective resin (BSR) DOWEX XUS 43594.00. In this process, BSR slurry with boron adsorbed on it is fed into the DD feed compartment. It was assumed that there are always some minute amounts of borate in the feedwater at equilibrium with the BSR. These amounts were subject to transport into the receiving solution as a result of Donnan dialysis, which should ultimately result in complete boron removal from the BSR. The net effect of the process would be a regenerated resin in the chloride form and boron (borate)-rich receiving solution. As reported by Bryjak et al. (2007), considerably high boron fluxes were observed during the course of a DD regeneration of boron containing BSR. Boron desorption was found to be the phenomena that governs kinetics of the boron transport in the process.

Unfortunately the tentative, mostly mechanistic report on DD boron removal presented in this chapter does not provide much information about the effectiveness of boron removal from water nor its final concentration. It seems that a lot of work

needs to be done to enhance the kinetics of the diffusive transport of borate during DD.

Cross-References

- [Boron Reduction](#)
- [Boron Removal by Electrodialysis](#)
- [Boron Removal by Reverse Osmosis](#)

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Breakthrough Pressure

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The pressure required for a liquid to enter the membrane pore is called breakthrough pressure. This parameter is of practical relevance as the membrane will not work properly if liquid enters the pores reducing in this way the contact efficiency. Breakthrough pressure can be estimated by using the Young-Laplace equation

$$P = \frac{-2\sigma \cos \theta}{r}$$

where σ is the liquid surface tension, θ the contact angle, and r the radius of membrane pore. It can be seen that high breakthrough pressure can be obtained by using liquids with high surface tension, by reducing the pore size, and by increasing the contact angle. However, there are practical limitations. For example, most of the physical solvents used for bulk CO₂ removal have low surface tensions, and the reduction in the membrane pore size beyond certain limit results into reduced transport of the gas through the membrane due to diffusion limitations. The higher contact angle for a given solvent is favored by the membrane material having low surface energies.

In order to give an idea, a hydrophobic polypropylene membrane with a pore size of 0.05 μm has a breakthrough pressure larger than 1 MPa (Wiesler 1996).

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Breath Figure Membranes

► [Honeycomb Membrane Structure](#)

BTEX Removal by PV on Polymeric Membranes

► [Toluene Removal by PV on Polymeric Membranes](#)

Buffer Displacement in Diafiltration

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Buffer displacement involves the use of diafiltration to replace the solvent (non-product) fraction of a macromolecular solution, with a buffer. The basis of the operation is that the solvent, including low molecular weight impurities,

passes through the membrane, while the solute (product) is retained. Suppose the solution can be viewed as a mixture containing a macromolecular product, A, and a micromolecular impurity, B. Now suppose that the buffer contains a desired component, C – a salt perhaps. Then, buffer displacement involves the reduction in the concentration of B while keeping the concentration of A constant and raising the concentration of C to the desired level. This can be done using constant volume (continuous) diafiltration, discontinuous diafiltration by dilution, or discontinuous diafiltration by volume reduction.

If constant volume diafiltration is used and B has an apparent rejection coefficient of zero, the concentration of B declines according to the expression (Cheryan 1998)

$$c_B = c_{B0} \exp(-V_b/V_s)$$

where V_b is the volume of buffer added while V_s is the (constant) volume of solution. Assuming that component, C, also has a rejection coefficient of zero, its concentration in the retentate solution increases according to the expression

$$c_c = c_{c0}(1 - \exp(-V_b/V_s))$$

where c_{c0} is the concentration of C in the buffer tank. If the product, A, has a rejection coefficient of 1.0, its concentration will remain unchanged.

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Buffer Flush in Diafiltration

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A buffer flush is simply the replacement of an impure, product-containing solution with buffer by subjecting it to ► [diafiltration](#).

The most common way of performing a buffer flush, at least in a membrane context, is to use constant volume (continuous) diafiltration in which a certain volume of buffer is added to a given volume of impure solution while that solution undergoes batch ultrafiltration, all the while keeping the solution volume constant.

The greater the ratio of buffer volume (V_b) to solution volume (V_s) (► [Diafiltration Factor](#)), the greater will be the reduction in undesired impurities. For example, if an impurity has a rejection coefficient of 0.2 and the diafiltration factor is 5×, the reduction in impurity concentration is given by (Foley 2013)

$$c/c_0 = e^{-(1-\sigma)V_b/V_s} = e^{-5(1-0.2)} = 0.018$$

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Bulk Biotech Industry

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The term “bulk biotech industry” is referring to the use of biological processes on industrial scale to produce bulk products. Examples of products from the bulk biotech industry are antibiotics, enzymes, organic and amino acids, vitamins, bioalcohols, and biopolymers. One of the earliest biotechnological processes adopted by humans is the production of alcohol by fermenting fruits around 5000–6000 years ago. The production of lactic acid by Pasteur in 1857 is often considered to be the beginning of modern biotechnology followed by the industrial scale production of citric acid by Pfizer in 1923 (Chotani et al. 2007). The first wave of biotechnology started with the discovery of penicillin by Fleming

in 1928 paving the way for the industrial scale production of antibiotics and amino acids. The discovery and increased understanding of the DNA created the foundation to use molecular engineering to recombine DNA leading to the second wave of biotechnology processes in the 1980s. The current third and so far final wave of biotechnology – the white biotechnology – aims to replace the C_2/C_3 chemistry based on fossil fuels such as oil and gas by biotechnological processes. It is foreseen that in the near future, up to 20 % of all chemical products with a market value of approx 250 € billion will be produced by biotechnology. Approximately 60 % of the products produced by white biotechnology will be intermediated chemicals used in the pharmaceutical industry, and the remaining 40 % will be biopolymers and special chemicals for various industries (Festel et al. 2004).

Since the 1970s, cross-flow membrane processes have established themselves in the downstream processing of the biotechnology industry for the recovery and purification of the products. It is foreseen that membrane processes will also play an important role in white biotechnology and the related concept of biorefineries. Similar to petroleum refineries, biorefineries are aiming for the full utilization of biomass for the simultaneous production of biofuels, biochemicals, heat, and power (Axegård 2005). The integrated production of biomaterials can be based on, e.g., sugar, starch, and cellulose-based feedstock and as such extend current sugar, starch, and pulp factories. Membrane processes as highly selective and energy-saving processes are well suited to play an important part in biorefineries and thus the white biotechnology.

The key membrane technologies for the bulk biotech industry are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Other membrane technologies such as membrane contactors (MC), electrodialysis (ED), pervaporation (PV), and vapor permeation (VP) plus membrane bioreactors for continuous fermentation are less established but have, nevertheless, the potential to become increasingly important.

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Bulk Liquid Membrane

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Bulk liquid membrane (BLM) consists of a bulk aqueous feed and receiving phases separated by a bulk organic, water-immiscible liquid phase. The feed and receiving phases may be separating from the LM by microporous supports or may be without supports (layered BLM).

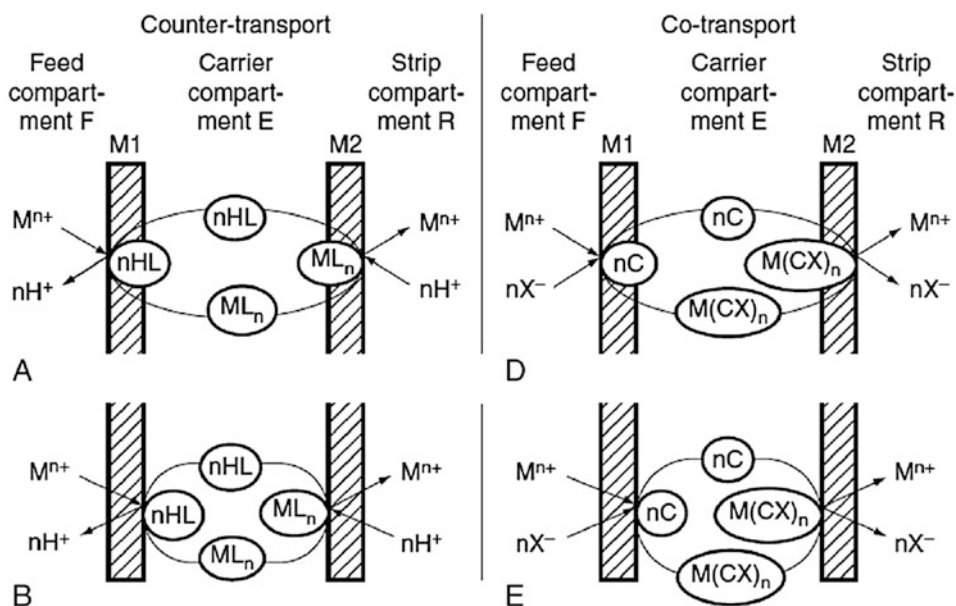
Many technologies that were developed and tested in the last two decades have to be included in the BLM group. These are hybrid liquid membrane (HLM), hollow-fiber liquid membrane (HFLM), hollow-fiber-contained liquid membrane (HFCLM), pertraction, flowing liquid membranes (FLM), membrane-based extraction and stripping, multimembrane hybrid system (MHS), and membrane contactor systems. All these systems are based on membrane-based nondispersive (as the means for blocking the organic reagent from mixing with the aqueous feed and strip solutions) selective extraction coupled to permselective diffusion of solute-extractant complexes and selective stripping of the solute in one continuous dynamic process (see Fig. 1). A great number of terms for similar bulk LM processes confuse the readers. The terms vary by membrane type used (hollow fiber, flat neutral, ion-exchange sheets) or by module design. All abovementioned bulk LM processes with

water-immiscible organic liquid membrane solutions may be unified under the term bulk organic hybrid liquid membrane (BOHLM) systems (for more details, see Kislik 2010a).

Bulk LM processes with water-soluble carriers are defined as bulk aqueous hybrid liquid membrane (BAHLM) systems (for more details, see Kislik 2010b). Regenerable water-soluble polyionic complexants are used as suitable aqueous liquid membrane carriers. These polyelectrolytes typically have a very high effective concentration of charged groups and could constitute highly selective complexants. The BAHLM technology is based on a combination of liquid membrane (LM) process and dialysis (D) in the case of neutral hydrophilic membranes or Donnan dialysis (DD) in the case of ion-exchange membranes used.

BOHLM and BAHLM technologies achieve the necessary transport and selectivity characteristics to have potential for commercial applications. Applications of the BOHLM processes are mainly in metal separation, wastewater treatment, biotechnologies, drugs recovery-separation, organic compounds, and gas separation. Selective separations of alkali, alkali earth, rare earth, heavy metal ions, precious metals, etc., are studied by many authors using all above-described techniques. Recovery and separation of carboxylic and amino acids from fermentation broth have been tested using layered BLM, rotating, creeping, spiral-type FLM, HFLM, HLM, and MHS-PV techniques of the BOHLM processes. Separation of ethylene, benzene, propanol, olefin, and aromatic amines from organic liquid mixtures and of volatile organic compounds (VOC) and phenol from wastewater was investigated using a rotating film module, spiral-type FLM, and hollow-fiber and layered LM techniques. High separation factors ($>1,000$) in pilot- and industrial-scale experiments were found. In the last two decades, BOHLM techniques were intensively used in analytical chemistry for separation and preconcentration of metals, organic acids, organic, and pharmaceutical compounds.

BAHLM is a new technology and few studies are known up to date. In metal separations copper-cadmium recovery from chloride aqueous solutions and cadmium, copper, and zinc separation



Bulk Liquid Membrane, Fig. 1 Schematic transport models of a bulk organic hybrid liquid membrane (BOHLM) system with **a, d** hydrophobic membranes and **b, e** hydrophilic or ion-exchange membranes

from wet-process phosphoric acid are studied. BAHLM systems were tested for the separation of carboxylic acids such as lactic, citric, and acetic or their anions. Continuous separation of different isomeric mixtures of organic compounds has been studied by means of a hollow-fiber-contained liquid membrane, HFCLM.

In recent years, integrated hybrid systems incorporating two or more functions in one module, for example, biotransformation and separation, become of great interest to researchers. The BOHLM systems, integrating reaction, separation, and concentration functions in one apparatus (bioreactor) attracted great interest in the last few years. Bioreactors combine the use of specific biocatalyst for the desired chemical reactions, with repeated or continuous application of it under very specific conditions. Such techniques were termed hybrid membrane reactors.

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Butanol-Water Mixtures: Separation by Pervaporation

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Because of the shortage of crude oil and the environmental requirement, the utilization of renewable resources for energy production, such as using the potential acetone-butanol-ethanol (ABE) fermentation process to produce butanol as a biofuel, has been receiving increased attention in recent years. However, the fermentation

process suffers from severe inhibition due to the high toxicity of butanol to microorganisms even at low concentrations ($4\text{--}6\text{ g}\cdot\text{L}^{-1}$). In order to eliminate the inhibition, in situ product recovery systems have been developed (Vane 2005). Pervaporation (PV) is considered to be a particularly promising recovery technique, because of its general advantages in energy saving and environmental issue, particularly no medium ingredients removed from the fermentation broth and no harmful effects on microorganisms.

The hydrophobic pervaporation membranes used for butanol recovery and concentrate include: polydimethylsiloxane (PDMS) and its modified copolymer and mixed matrix membranes, liquid membrane, poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membrane, poly(ether block amide) (PEBA) membrane, polypropylene (PP) membrane, polytetrafluoroethylene (PTFE) membrane, etc. (Vane 2005; Liu et al. 2011). PDMS, as the most typical hydrophobic polymeric membrane, is widely investigated and proved to be stable and prospective for industrial applications. The operating parameters of PV, including feed temperature (T), feed concentration (C), feed flow rate and permeate pressure (P), etc., have significant impacts on membrane performance. Take the PDMS/ceramic membrane, for example, flux increased as temperature increased, while the separation factor decreased slightly. As the butanol concentration increased, the total flux increased while the separation factor changed slightly. The total flux increased with the flow rate, but the separation factor changed little (Liu et al. 2011).

Pervaporation using hydrophobic membranes might not be enough for concentrating butanol for direct reuse. Hydrophobic membranes were preferred for concentrating butanol when the

concentration of butanol is low. As an alternative, when the butanol concentration is high and the water content is low, the hydrophilic membranes should be used for the water removal, so that the pervaporation process is economic for butanol production.

The hydrophilic pervaporation polymeric membranes used for dehydration of butanol-water mixtures include: poly (vinyl alcohol) (PVA) membrane, polyimide membrane, chitosan membrane, sodium alginate membrane, polyelectrolyte, etc. (Chapman et al. 2008). PVA is the most commonly used hydrophilic polymeric membrane, but it often shows a lack of chemical, mechanical, and thermal stability. In recent years, the PI membrane began to be used for dehydration because of its excellent mechanical and thermal stability. The main inorganic membranes used for butanol dehydration are silica membrane (Verkerk et al. 2001) and A-type zeolite (NaA) membrane (Morigami et al. 2001).

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Cadmium Rejection by NF

► Cadmium Separation by NF

Cadmium Separation by Liquid Membranes

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Cadmium separation by liquid membranes:

Cadmium occurs as a minor component in the zinc ores. It has many common industrial applications. Despite wide applications, cadmium is known to be a toxic element, and the occupational exposure is by inhalation of fumes and ingestion of soluble cadmium compounds. This metal is an environmental hazard. Therefore, due to its industrial, chemical, or environmental importance, it must be separated prior to determination or recovery from original matrices. Liquid membranes broadly classified into bulk, emulsion, and supported liquid membranes (SLM) have found wide applications for separation of metal species (including cadmium) during the recent years (Dalali et al. 2012; Kumbasar 2008; Carletto

et al. 2009). Bulk liquid membranes (BLM) usually consist of two aqueous feed and stripping phases, separated by a water-immiscible liquid membrane phase with a relatively small surface area. Emulsion liquid membranes have a very high surface area per unit of volume and low thickness. The problem is that the vehicles have to be produced before the process; they have to be stable enough to have minimum leakage, but still not very stable so that they could be destroyed after the separation. In SLM, usually organic liquid is imbedded in small pores of a polymer support and is kept there by capillary forces. If the organic liquid is immiscible with the aqueous feed and strip streams, SLM can be used to separate the two aqueous phases.

Hollow fiber modules are usually more expensive, but they offer much higher surface area per unit of module volume. In the simplest case, the organic solvent with a carrier is filling the pores of the microporous walls of hollow tubes. Transport with liquid membranes is a kinetic process and controlled by diffusion rate of analyte through the membrane. The membrane separation processes operate at ambient temperature and thus use less energy than thermal separations. The basic concept for a metal cation to transport through a liquid membrane (regardless of membrane type) is its conversion to (i) an uncharged hydrophobic species in the feed-membrane phase interface and (ii) a hydrophilic species in the

membrane-stripping phase interface. Therefore, the metal ion should either form an ion pair complex or a chelate in the presence of a hydrophobic organic salt or chelating agent as carrier in the membrane phase to fulfill such requirement. On the other hand, the selectivity of transport or separation efficiency depends upon the stability of metal complexes (ionic or neutral) or salts formed in feed, membrane, and stripping phases, which in turn is affected by the type and concentration of salt in the two aqueous phases and of carrier (extractant) in membrane phase. The separation of cadmium by a BLM as a chloride complex via its ion pair formation with trioctyl methyl ammonium chloride (Aliquat 336) in benzene as organic carrier into EDTA solution as stripping phase (Dalali 2012) was influenced by concentration of NaCl in the feed phase, concentration of carrier (Aliquat 336), and type and concentration of stripping solution (EDTA). The rate of transport depends upon the area and thickness of membrane or the interfaces. The larger the surface area and the less the thickness of interface, the faster will be the mass transfer. The effective separation of cadmium is achieved in the above, e.g., within 4 h, while the similar separation by an ELM has been achieved within 10 min time (Kumbasar 2008), due to the larger surface area and the thinner interface in ELM.

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Cadmium Separation by NF

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Synonyms

[Cadmium rejection by NF](#); [Cadmium wastewater treatment by NF](#)

Heavy metals present in wastewaters cause serious problems to human beings and other living organisms. Different methods are available to separate heavy metals such as precipitation, coagulation, flocculation, ion exchange, electro-dialysis, reverse osmosis (RO), nanofiltration, etc. (Wang et al. 2007). Nanofiltration (NF) is relatively new and it falls between RO and ultra-filtration (UF). NF can be operated at much lower pressures than RO. NF can achieve high removal of divalent and multivalent ions, but only moderate removal of monovalent ions is possible (Wang et al. 2006). Nanofiltration can be characterized by molecular weight cutoff (MWCO) between 200 and 1000 due to the pore diameter range of 0.5–2 nm, and also NF membranes are either positively charged or negatively charged. NF permits the retention of small molecules in the molecular mass range of 200–2000 Da (Wang et al. 2011). Cadmium is mainly toxic to the kidney and can also cause bone demineralization. Cadmium is one of the endocrine disruptor compounds (WHO 2013). The International Agency for Research on Cancer (IARC) has classified cadmium as a human carcinogen (Group 1) on the basis of occupational studies (European Food Safety Authority 2009). Cadmium is an odorless, silver-white, blue-tinged malleable metal or grayish-white powder with an oxidative state of +2, and it forms salts such as sulfate and nitrate. In the environment, cadmium is not usually present as a pure metal but as a mineral, such as cadmium oxide, cadmium chloride, cadmium sulfate, cadmium sulfide, etc. The chlorides and sulfates are

Cadmium Separation by NF, Table 1 Summary of the reflection coefficients for cadmium separation by NF-300 membrane

Feed concentration, mg/L	Reflection coefficient						
	CdSO ₄	NiSO ₄	CdCl ₂	NiCl ₂	CdCl ₂	NiSO ₄	CdCl ₂
5	0.9863	0.9951	0.8861	0.9051	0.8749	0.9961	----
50	0.9842	0.9938	0.8567	0.8753	0.8455	0.9905	0.7556
100	0.9822	0.9924	0.8233	0.8419	0.8121	0.9864	0.7227
150	0.9801	0.9914	0.7921	0.8106	0.7809	0.9849	0.7197
200	0.9781	0.9897	0.7620	0.7805	0.7508	0.9834	0.6749
250	0.9760	0.9883	0.7177	0.7363	0.7065	0.9819	0.6644

most easily dissolved in water. Cadmium metal itself does not disappear from the environment, but it may change forms; hence, knowing the particular form of cadmium is very important when determining the risk of potential adverse health effects (US Department of Health and Human Services, July 1999). When RO and NF are compared in separating cadmium from wastewater, the results showed that RO was capable of treating wastewater with an initial concentration of 500 ppm and reducing the ions concentration to about 3 ppm (99.4 % removal), whereas the average removal efficiency by NF was 97 % (Qdais and Moussa 2004). Cadmium separation from wastewaters by NF assumes importance due to its low-energy consumption and ease of operation. By using an NF-300 membrane system (Murthy and Chaudhari 2008, 2009; Chaudhari and Murthy 2010), the separation of cadmium from dilute aqueous solutions having different cadmium salts was reported. In wastewaters generally cadmium is not alone but is present with other metals such as nickel. Separation data were reported for CdCl₂-water system, CdCl₂-NiCl₂-water system, CdSO₄-NiSO₄-water system, and CdCl₂-NiSO₄-water system (Murthy and Chaudhari 2008, 2009; Chaudhari and Murthy 2010). The separation capability of an NF membrane can be related with its reflection coefficient. If reflection coefficient is zero, it means the separation of a solute is zero, and similarly if it is one, the separation is 100 %. Table 1 (Murthy and Chaudhari 2008, 2009; Chaudhari and Murthy 2010) shows the separation capability of NF-300 membrane at different feed concentrations. All the experiments are performed at a pH of 5.0 ± 0.1,

feed rate 15 L/min, and applied pressure 4–20 atm. It can be seen from Table 1 that the reflection coefficient decreases with increase in feed solute concentration. It is observed that the reflection coefficient for each salt increases with co-ion valency. Recently, modeling of cadmium removal by nanofiltration using genetic programming was reported (Okhovat and Mousavi 2012). A mechanism related to cadmium salt transport through a nanofiltration membrane was proposed by Garba et al. (2000), and it was found that in most cases convection plays the most important role.

Cross-References

- Nanofiltration (Transport Phenomena)
- NF Membrane Characterization Methods
- NF Membranes
- Nickel, Recovery of

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Cadmium Wastewater Treatment by NF

► Cadmium Separation by NF

Cadmium, Recovery of

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Recovery of cadmium from aqueous effluents by membrane operations. Cadmium is a metal

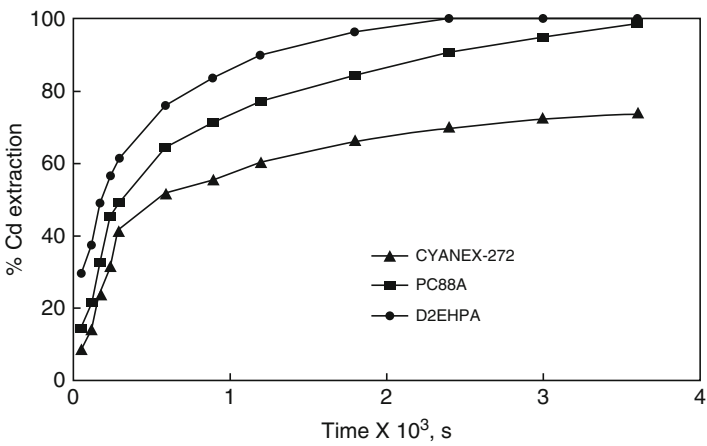
found in the earth's crust at concentrations ranging from 0.1 to 5 ppm, primarily as sulfide minerals in association with zinc ores, zinc-bearing lead ores, and/or complex copper-lead-zinc ores. The salts of cadmium chloride and cadmium sulfate are soluble in water. Most of the cadmium is extracted through mining. Cadmium is mainly used in batteries (83 %), pigments (8 %), coatings and platings (7 %), stabilizers for plastics (1.2 %), nonferrous alloys, photovoltaic devices, and other uses (0.8 %). Hence, naturally cadmium is mainly recovered from used batteries (Toxicological profile for cadmium 2012). Cadmium is recovered from spent NiCd batteries, copper-cadmium alloy scrap, some complex nonferrous alloy scrap, and cadmium-containing dust from electric arc furnaces (EAF). In 2006, the US steel industry generated about 0.7 million tons of EAF dust, typically containing 0.003–0.07 % cadmium (Mineral Commodity Summaries 2007). Recently, membrane separations are being used to recover/extract the cadmium from different waste streams. Cadmium present in the dust form was most efficiently collected by membrane filters (United Nations Environment Programme: Chemicals Branch 2010). Cadmium, along with other metal ions, was recovered from acidic leach solutions by emulsion liquid membrane (ELM) using trioctylamine (TOA) as extractant (Kumbasar 2009). The results showed (Kumbasar 2009) that up to 98 % cadmium recovery was possible after 10 min contact time by using ELM (Table 1). Jha et al. (2012) and Safarzadeh et al. (2007) show the possibility of extraction and separation of cadmium from different solutions containing other metallic ions. The cadmium extraction efficiencies of three phosphoric acid derivatives such as bis-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), and bis-(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272) have been reported using supported liquid membrane (SLM) (Fig. 1) (Parhi et al. 2009). Also, several researchers reported the recovery of cadmium by SLM with different extractants (He et al. 2007). Polymer-enhanced ultrafiltration (UF) and nanofiltration

Cadmium, Recovery of, Table 1 Effect of extractant concentration on the extraction rate of Cd (Span 80: 6 %; kerosene: 86–92 %; stripping solution: 18 mL NH₃ solution of 6 M; mixing speed: 250 rpm; Cd concentration of feed solution: 100 mg/L; HCl concentration of feed solution: 1.0 M; phase ratio: 3/5; feed solution: 250 mL) (Reproduced with permission from Elsevier)

Extractant concentration, %	C/C_0				
	0 min	2 min	4 min	6 min	10 min
2	1	0.121	0.03	0.01	0.01
4	1	0.101	0.01	0.01	0.01
6	1	0.09	0.01	0.01	0.01
8	1	0.083	0.01	0.01	0.01

Cadmium, Recovery of,

Fig. 1 Percentage extraction of Cd at different times with D2EHPA, PC-88A, and Cyanex 272. Experimental conditions: pH 7.5, 600 mol/m³ extractant in membrane phase, 900 mol/m³ H₂SO₄ in strip solution, and 120 mL/min flow rate (Reproduced with permission from Elsevier)



(NF) are also being used to recover cadmium with encouraging results (Cañizares et al. 2008; Ennigrou et al. 2009; González-Muñoz et al. 2006).

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Capillary

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The word **capillary** originated from the Latin adjective *capillaris*, which means “pertaining to the hair.” Possibly, the scientific phenomenon was first observed between contiguous hairs, for example, within a paintbrush.

In medicine and biology, capillary is the smallest of a body’s blood vessel and is part of the microcirculation. The word capillary, in the nonmedical sense, means narrow tube.

In membrane science the noun capillary is both used to name the inner spaces of a porous media and to specify a typical membrane (see ► [Capillary Membrane](#)). The classification of porous membrane filter types is mainly based on the nominal diameter of the capillaries in the membrane. Artificial capillaries in porous media are produced by interfacial polymerization, or the natural porosity in solid materials is adjusted to the desirable nominal diameter. The shape and size of the pores in the membrane are very diverse.

The pore theory of membrane transport through the capillaries considers that both convection and diffusion contribute to solute transport across the porous membrane, the two processes being impeded by steric hindrance at the entrance of the pores and by frictional forces within the pores; the same steric hindrance and frictional resistance terms were used in the convection and diffusion terms of the solute transport equation (Pappenheimer et al. 1951).

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Capillary Flow

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Capillary flow means the movement of the fluid in the internal gaps and on the surface of the solid material, where the driving force is the molecular interaction between the solid and fluid material (see ► [Capillary Force](#)). If the fluid is incompressible and Newtonian, the flow is laminar through a pipe of constant circular cross section that is substantially longer than its diameter, and since there is no acceleration of fluid in the pipe, the total flow rate (Q) could be estimated according to Poiseuille’s law (Briant et al. 1989):

$$Q = \frac{d^4 \pi \cdot \Delta P}{128 \cdot \mu \cdot L}$$

where d represents capillary diameter, ΔP is the total pressure drop along the channel, μ is the fluid viscosity, and L represents the capillary length.

For velocity calculation, let us consider a laminar horizontal flow through a straight circular channel of length L and a radius r . The mean flow velocity u through the channel is given by (Landau and Lifshitz 1987):

$$u = -\frac{r^2}{8\mu} \frac{\Delta P}{L}$$

where ΔP is the total pressure drop along the channel and μ is the fluid viscosity.

In the general case of two immiscible fluids:

$$u = -\frac{r^2}{8\mu_{eff}} \frac{\Delta P - P_c}{L}$$

where

$$\mu_{eff} = \frac{x}{L} \mu_w + \frac{L-x}{L} \mu_a$$

is the effective viscosity; μ_w and μ_a are viscosities for phase w and phase a fluids, respectively; x is the location of the interface measured from the inlet; P_c is the capillary pressure across the interface; and a_0 is a constant associated with the channel cross-sectional shape.

Assuming that the fluid system is in static equilibrium, the capillary pressure at an interface in a circular channel is (Young-Laplace eq.):

$$P_c = \frac{4\gamma \cdot \cos \theta}{d_c}$$

where γ represents the interfacial tension, θ is the contact angle, and d_m represents the capillary diameter.

Since the determination of the number of active capillaries during membrane filtration is very difficult, statistical approach from Darcy can be applied basically. Darcy's law is a simple proportional relationship between the instantaneous discharge rate through a porous medium, the viscosity of the fluid, and the pressure drop over a given distance:

$$Q = \frac{-k \cdot A \cdot \Delta P}{\mu \cdot L}$$

where Q is overall flow rate, k represents permeability of the medium, A is the cross-sectional area to flow, ΔP is the pressure drop, μ represents viscosity, and L is the length over which the pressure drop is taking place.

Due to the concentration polarization phenomenon, gel layer forming, membrane fouling, and pore blocking, the global model was further developed for different membrane techniques, see, e.g., resistances-in-series model or solution-diffusion model.

The diffusion of gasses, liquids, and solids in solids is quite important in mass transfer operations. The diffusion is greatly affected by the size and shape of pores and capillaries. For example, in porous solids, the effective diffusion of salts (A) in water (B) is described as:

$$D_{\{-A, \text{eff}\}} = D_{AB} \frac{\epsilon}{k_2}$$

where D_{AB} represents the diffusivity of salt in water, ϵ is the porosity, and k is a correction factor for the distance (when it is nonlinear; general value = 1.2–2.5).

The diffusion of a liquid in capillaries has three types: Knudsen diffusion, molecular (Fick's) diffusion, and transition region diffusion (Geankoplis 1972).

The power-law is an improvement to the Poiseuille's equation by generalizing the flow to include non-Newtonian effect. The beauty of this model is its simplicity. However there are other aspects of the flow properties of fluids which this model fails to examine, one of them being the presence of yield stress (Mazumdar 1992)

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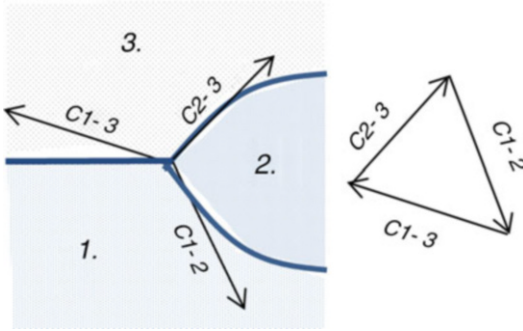
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Capillary Force

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Capillary force is the force which generates movement of a liquid along the surface of a solid caused by the attraction of molecules of the liquid to the molecules of the solid. For example, molecules of water are naturally attracted to each other and form temporary hydrogen bonds with each other; their attraction for each other on the surface of a liquid, for example, gives rise to surface tension. But they are also attracted in a similar way to other molecules, called hydrophilic molecules, such as those in the sides of a narrow glass tube inserted



Capillary Force, Fig. 1 Contact of three fluids

into water. These attractive forces can draw water up against the force of gravity to a certain degree.

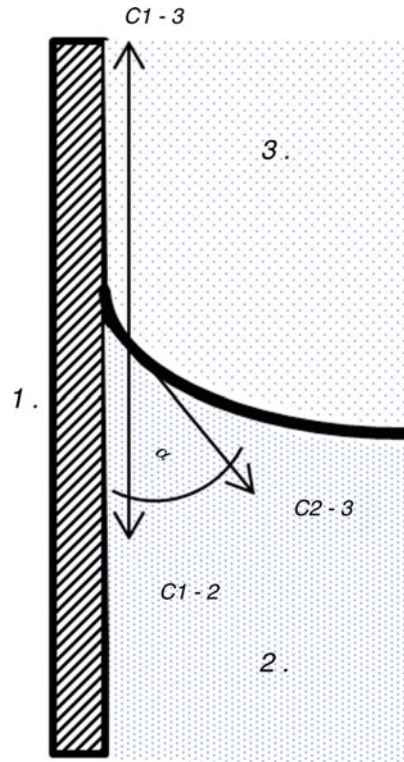
Where three different fluid interfaces are contacting each other along one line, equilibrium exists only when the vector polygon of the stresses is closed. This requirement determines the angle between the edges of disjunctive surfaces (Pattantyús 1961) (Fig. 1).

Sometimes $|C1-3| > |C1-2| + |C2-3|$ occurs. Because vector $C1-3$ is always larger, equilibrium is not possible; therefore, fluid no. 2 is permanently moving on the no. 1 and 3 fluid interface. For example, mineral oil unfolds the water surface even to molecule thick layer when the available area is sufficient.

One angle of the vector triangle is given in cases where instead one of the liquids a solid material presents. In Fig. 2 this angle is 180° . The requirement of equilibrium: $C1-3 = C2-3 + C1-2 \cdot \cos\alpha$.

In case of solid particle or material, $|C1-3| > |C1-2| + |C2-3|$ can also exist sometimes, and no. 2 liquid could totally cover the solid surface (1). This movement is usually limited by impurities on the solid surface. For mercury–air–glass system, $|C1-3| < |C2-3|$ and $\alpha > 90^\circ$.

The Young–Laplace equation is a nonlinear partial differential equation that describes the capillary pressure difference or capillary force sustained across the interface between two static fluids, due to the phenomenon of surface tension or wall tension, although usage on the latter is only applicable if assuming that the wall is very thin. The Young–Laplace equation relates the



Capillary Force, Fig. 2 Contact when one solid phase is present next to two fluids

pressure difference to the shape of the surface or wall, and it is fundamentally important in the study of static capillary surfaces. It is a statement of normal stress balance for static fluids meeting at an interface, where the interface is treated as a surface (*scpacp*).

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Capillary Membrane

► [Capillary Membrane Module](#)

Capillary Membrane Module

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Synonyms

Capillary membrane; Capillary module

A number of different membrane modules based on capillaries are possible, and all are based on the same membrane geometry with different dimensions as shown in Fig. 1.

The capillary membrane module consists of a large number of capillaries assembled together in a pressure vessel similar as a hollow fiber module (Mulder 1997). The free ends of the capillaries are potted with agents such as epoxy resins, polyurethanes, or silicone rubber. The capillaries are self-supporting. Two types of module arrangements can be distinguished (Mulder 1997):

- Where the feed passes through the bore of the capillary
- Where the feed enters the module on the shell side

The choice between the two concepts is mainly based on the application where parameters such as pressure, pressure drop, type of membrane available, etc. are important. Depending on the

concept applied, asymmetric capillaries are used with their skin on the inside or on the outside (Mulder 1997).

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Capillary Membranes

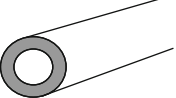
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Artificial capillary membranes are one type of the tubular-shaped membrane filters. With capillary membranes, the membrane serves as a selective barrier, which is sufficiently strong to resist filtration pressure. Because of this, the flow through capillary membranes can be both inside out and outside in.

The diameter of capillary membranes is much smaller than that of tubular membranes, namely, 0.5–5 mm. Because of the smaller diameter, the chances of plugging are much higher with a

Capillary Membrane Module, Fig. 1 Available types of capillary membranes adapted from Scholz et al. (2011)

Hollow fiber membranes		outer D ~ 0.08-0.8 mm inner D ~ 0.04-0.5 mm
Capillary membranes		inner D ~ 0.5-5 mm outer D ~ 0.8-7 mm
Tubular membranes		outer D ~ 5 -25 mm



Capillary Membranes, Fig. 1 Ceramic capillary membrane (Source: www.kerafol.com)

capillary membrane. A benefit is that the packing density is much greater. The first capillary membrane was fabricated from polymers, but nowadays the technology development enables the production of inorganic capillary modules (Fig. 1).

Description of a Capillary Membrane Module

A complete description of a membrane module requires the simultaneous solution of local transport equations that describe the flow and transport conditions. In a capillary membrane module with a permeable membrane wall, three regions of flow should be considered: flow in the lumen, flow within the membrane matrix, and flow in the extracapillary space. The pressure distribution in the membrane is determined by application of the overall balance of linear momentum. The utilization of this conservation principle is complicated by the fact that an external force must be applied to keep the polymer membrane stationary. In order to describe the behavior of a membrane module, three submodels are required: two that describe the transport on either side of the membrane and a third model that characterizes the separation properties of the membrane and any porous support material (Nagy 2012).

Membrane Development

Besides polymeric and ceramic capillary membranes, other types are also developing due to its

benefits. For example, supported zeolite membranes have been synthesized under microwave heating in order to reduce synthesis time in the work of Sebastian et al. (2010) to prevent support dissolution and to reproducibly obtain a thin defect-free zeolite layer. The MFI-type zeolite membranes were synthesized on ceramic capillaries, with a high membrane surface area-to-volume ratio ($>1,000 \text{ m}^2 \text{ m}^{-3}$), which is by far higher than that of classical tubular supports ($<500 \text{ m}^2 \text{ m}^{-3}$).

In a study of Zhu et al. (2010), alumina microfiltration membranes were prepared on the inner surface of alumina capillary support (outer diameter, 4 mm; inner diameter, 2.5 mm) by a dip-coating method. Scanning electron microscopy (SEM) observation, gas bubble pressure (GBP) method, and membrane permeation test were carried out to evaluate membrane performance. Two major effects in preparation of crack-free membrane, capillary filtration, and film coating upon the thin support were studied.

Bonyadi and Mackley (2012) reported the experimental results for the processing of micro-capillary film (MCF) membranes. MCFs are films with embedded multiple hollow capillaries and can be considered as a hybrid geometry between flat sheet and hollow fibers. Compared to the conventional membrane geometries, MCFs potentially provide a higher surface area per unit volume, better mechanical strength, ease of handling, and more efficient module fabrication. MCF membranes were fabricated out of ethylene vinyl alcohol (EVOH) copolymer through a solution extrusion followed by a nonsolvent induced phase separation (NIPS) process.

Solvent resistant nanofiltration (SRNF) is a membrane separation process allowing for an efficient separation of small molecules of 200–1,000 g mol⁻¹ from organic solvents. The application of SRNF in industry applications is currently hindered by a limited choice of SRNF membranes and configurations. In the work of Dutczak et al. (2011), SRNF composite capillary membranes made of an α -alumina support and a selective poly(dimethylsiloxane) (PDMS) top layer were prepared and studied. We combine the advantages of a ceramic support such as high

mechanical, thermal, and chemical stability with very good separation properties of the PDMS coating.

Possible Applications

The number of practical applications of capillary membranes is also expanding. A new combined method is reported to localize the sites of enzyme immobilization and to determine its catalytic activity on a polymeric capillary membrane reactor activity (Mazzuca et al. (2006)). β -Glucosidase from olive fruit was selected as enzyme model because of its suitable relevance in the industrial processing of foods, in biotechnology, and in pharmaceuticals and for its activity against the synthetic substrate 5-bromo-4-chloro-3-indolyl- β -D-glucopyranoside which develops an insoluble dyed product. The enzyme was physically immobilized within 30 kDa cutoff capillary polysulfone membranes, and results obtained by means of a polyclonal antibody against β -glucosidase and the synthetic substrate clearly showed a coherent localization of the immobilization enzyme sites and its activity.

Commercial flat sheet membranes were compared to capillary one's (Van der Bruggen et al. 2003). For the capillary membrane, the water flux could, however, easily be increased and maintained at a stable level by a combination of forward flushing and airflushing, which is not possible with the flat sheet membranes. Furthermore, the water permeability for the capillary membrane was 3–15 times higher than for the commercial flat sheet membranes, which leads to lower operating pressure and a correspondingly lower energy consumption. For the capillary membrane, rejections of organic and inorganic compounds were satisfactory to reach for COD and conductivity standards in one step starting from the surface water. Rejections for most flat sheet membranes were comparable to the rejections obtained with the capillary membrane, but the rejection of ions was usually higher, except for the N30F and NF PES 10 membranes. Low ion rejections are advantageous for drinking water production because demineralization is avoided.

Suitability of capillary modules to the decolorization of both synthetic and actual dye solutions by ultrafiltration was investigated as well. The process involved capillary membranes made of polysulfone and modified polysulfone. Membrane modules (UFTA PS10, UFTA PS30, and UFTA PSA50) of various molecular cutoffs were applied (Majewska-Nowak et al. 1996).

Investigations concerning the application of ceramic and capillary microfiltration and ultrafiltration membranes for the purpose of treatment of natural water were carried out by Bodzek and Konieczny 1998. The effectiveness of ultra- and microfiltration was assessed by volumetric measurements of the permeate flux as well as by microbiological and physicochemical analyses.

Analysis of oxygen permeation fluxes through Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) capillary membranes, fabricated via a phase inversion spinning technique using polysulfone as binder, showed a significant limiting role of the surface oxygen exchange kinetics. Within the studied temperature and oxygen partial pressure ranges, the activation of core and shell sides of the BSCF capillary with praseodymium oxide (PrOx) resulted in an increase in permeation rate of about 300 % (Kovalevsky et al. 2011).

Capillary membrane diffusion scrubber (CMDS) was scaled down to match with capillary electrophoresis (CE), a quick separation technique that requires nothing more than some nanoliters of sample and, when combined with capacitively coupled contactless conductometric detection (C4D), is particularly favorable for ionic species that do not absorb in the UV–vis region, like the target analytes formaldehyde, formic acid, acetic acid, and ammonium (Coelho et al. 2010).

Ceramic tube and ceramic capillary membranes and their effect on permeate flux, oil retention, and specific energy consumption were compared in the work of Gáspár et al. (2011). The results, obtained with a stable oil-in-water microemulsion as feed, demonstrated that the use of novel ceramic capillary membranes at optimal operating cross-flow velocity and transmembrane pressure is reasonable.

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Capillary Module

► Capillary Membrane Module

Capillary Tubes

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Def. (Engineering) A tube sufficiently fine so that capillary attraction of a liquid into the tube is significant. (General Physics) A glass tube with a fine bore and thick walls, used in thermometers, etc. (Medical) Glass capillary tubes are used for the collection of blood in a variety of healthcare settings, including hospitals, ambulatory care facilities, physicians' offices, blood donation facilities, and blood testing centers.

Basic Description

A capillary tube works by its being tension pulling between the circumference and the inner wall of the tube. The restriction and metering of the liquid will maintain pressure differential. See more at

► Capillary Force.

Capillary tubes can be made of different materials like plastic, glass, stainless steel, and ceramics.

Wall thickness of microhematocrit capillary tubes is 0.01 mm.

Applications

It can be a device used to measure kinematic viscosity. Kinematic viscosity is the time it takes for a fixed amount of fluid to move through a measured length of the capillary tube with gravity alone.

In Membrane Science once capillary tubes present in the filter media, they are called pores. Symmetric pore structure is usually formed by pressing and sintering, extruding and stretching, irradiation and etching, template leaching, or phase inversion. On the other hand, capillaries can be found in capillary membranes as well.

Capillary tubes are used in analytical applications, such as chromatography, gas and liquid lines, and measurement components in remote thermometer systems (with or without compensation).

An indispensable capillary tube is used for calculating blood clotting time or determining melting points.

Also a capillary tube is used in refrigeration and air-conditioning systems. It is a copper tube that has a small internal diameter. A capillary tube functions by dropping pressure due to its small internal diameter. The refrigerant leaves the condenser and enters the capillary tube and when it reaches the capillary tube falls in pressure and keeps the pressure constant. It limits the maximum amount of the refrigerant that can be charged in the refrigeration system.

Carbon Capture and Storage (CCS)

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Carbon capture and storage (CCS) is a proposed strategy to separate carbon dioxide from industrial gases and store that carbon on a geological time-scale. This is a response to the perceived threat industrial carbon dioxide emissions have in producing anthropogenic climate change (IPCC 2007). CCS is divided into three distinct stages, the capture of the carbon dioxide from the emission source, the compression and transportation of CO₂ to the storage site, and the final storage of CO₂ for long periods of time (IPCC 2005).

The capturing of CO₂ is predominately associated with large stationary point sources and in particular coal-fired power stations. The strategies to capture carbon emissions from these sources can be classified into three distinct approaches: post-combustion capture, oxy-fuel combustion, and precombustion capture (Table 1).

Post-combustion capture is the separation of CO₂ from flue gases after the combustion process.

This is primarily a separation of CO₂ from N₂, as well as water and other minor components, such as CO, SO_x, and NO_x. The separation process occurs at lower pressures, low CO₂ partial pressures, and often around ambient temperature. Oxy-fuel combustion is pure oxygen firing of the combustion process. This excludes N₂ from the combustion zone and produces a flue gas consisting of CO₂ and H₂O. Carbon capture is achieved through water removal. However, the very high flame temperature often dictates flue gas recycling, and critically this strategy requires the separation of high purity O₂ from air, which is commonly achieved through cryogenic methods. Precombustion capture is the gasification of the carbon-based fuel into synthetic gas, also called syngas, consisting of CO and H₂. This syngas is an important industrial feed gas that is used in a wide range of processes, such as Fischer-Tropsch synthesis. For power generation, H₂ production is often maximized through the water gas shift reaction, resulting in high-pressure gas mixtures of CO₂, CO, and H₂. Separation of CO₂ is achieved before H₂ undergoes combustion. This separation strategy takes advantage of the high pressure and CO₂ partial pressure before combustion.

Carbon capture has also been applied to other industrial applications, such as natural gas sweetening, for the removal of acidic gases to meet pipeline specifications, as well as in natural gas reforming for ammonia production.

A range of separation technologies have been applied to carbon capture, including solvent separation, membrane gas separation, adsorption technology, cryogenic separation, and mineral carbonation. The current commercial technology of choice is physical and chemical solvent technology, with membrane gas separation having been commercial proven in natural gas sweetening.

Transportation of captured CO₂ to the storage site is undertaken through shipping (low temperature and low pressure) or pipelines (high pressure and ambient temperature). The method of transportation is dependent on distance and geography between the source and storage sites.

Storage of carbon for extended periods of time can be achieved through geosequestration, deep ocean storage, or mineralization. Geosequestration

Carbon Capture and Storage (CCS), Table 1 Carbon capture strategy conditions and gas compositions

	Post-combustion	Oxy-fuel combustion	Precombustion
Pressure (bar)	1	1	30
Composition (mol. frac.)			
CO ₂	0.11	0.87	0.40
N ₂	0.62	–	–
H ₂	–	–	0.55
O ₂	0.04	0.05	–
H ₂ O	0.23	0.08	0.02
CO	–	–	0.03

is the injection of supercritical CO₂ into geological formations, generally sedimentary basin, over a kilometer underground. Importantly, the geological formation must contain a suitable reservoir rock, with high permeability and porosity for CO₂, as well as a seal rock above the reservoir that forms the necessary geological trap. Possible geological sites for CO₂ geosequestration include disused oil and gas fields, saline aquifers, as well as deep coal seams. Currently, CO₂ is geosequestered commercially as part of enhanced oil recovery procedures.

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Carbon Clothes in Fuel Cells

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Carbon cloth is used as gas diffusion layers (GDL) in fuel cells. The GDL is an essential

component in the fuel cell which performs several functions such as to distribute reactant gases, water management, and electrical conduction. Carbon cloth is one of the two preferred materials (other one is carbon paper) for GDLs in polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC).

Carbon cloth is commercially available in thickness of about 300–450 µm. Carbon cloth is made by weaving carbon fibers and therefore is more flexible and resilient than carbon paper-based GDL layers. Because carbon cloth is electrically conductive, it also provides pathway for current collection. Therefore carbon cloth GDL acts as electrical connection between the bipolar plate and the catalyst layer (reaction layer) where the electrons are liberated/consumed in the electrochemical reactions involved inside the fuel cell. Carbon cloth offers good porosity to allow easy passage of reactants (i.e., gas) to diffuse to the catalyst layer for more uniform reaction. The good porosity of carbon cloth also helps in the removal of products of the fuel cell reaction, i.e., water and oxygen depleted air, while the heat is transferred away from the reaction site to other components inside the cell. It is important to prevent the flooding of the GDL; therefore carbon cloth is made wet proof typically with a hydrophobic coating (e.g., PTFE or Teflon). Carbon cloths are often highly compressible, reaching up to 40–50 % compression when in a stack. This compression can significantly change their electrical and gas permeation properties and therefore careful consideration is required when using carbon cloth as a GDL.

Carbon Dioxide (CO₂) Separation by Membranes

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Carbon dioxide (CO₂) separation by membranes has been proposed for a range of carbon capture and storage strategies. To date, CO₂-selective membranes have only been commercialized for natural gas sweetening, though a range of membrane pilot plants are currently assessing the feasibility for CO₂ separation from syngas and flue gas. In all of these applications, the CO₂-selective membrane is based on nonporous polymeric membranes. These operate on the solution-diffusion mechanism and take advantage of the strong CO₂ solubility within the polymeric matrix relative to other gases, such as N₂ and H₂. In particular, glassy polymeric membranes are applied to CO₂ separation from flue gas and natural gas, because of the high permeabilities and selectivities possible for these types of polymers. While, for CO₂ separation from syngas, rubbery polymeric membranes are the focus, because these can provide the CO₂/H₂ selectivity needed for CO₂ separation. Molecular sieving and surface diffusion membranes based on porous inorganic and nanoporous carbon materials have been developed that are CO₂ selective. However, there is currently no industrial plant or pilot trials of these membranes.

The first CO₂-selective membrane to be commercialized was cellulose acetate, for the natural gas sweetening industry. Generally, these membranes are a combination of cellulose acetate, cellulose diacetate, and cellulose triacetate and have CO₂ permeabilities on the order of three to six barrer and CO₂/CH₄ selectivities of 25–40. Currently, cellulose acetate membranes make up to 80 % market share of membranes in natural gas processing, and modules of both spiral wound and hollow fiber designs can be purchased (Scholes et al. 2012). Cellulose acetate-based membranes are currently commercialized under the names Cynara[®] (part of Cameron) and UOP Separex[®] (part of Honeywell).

The second generation of CO₂-selective membranes are based on polyimides. These types of membranes generally display higher permeabilities and selectivities for CO₂ than cellulose acetate-based membranes. These have a CO₂ permeance range of 10–200 GPU and a CO₂/CH₄ selectivity range of 5–30. Polyimide modules are predominately hollow fiber design and have been commercialized by UBE Industries and Air Liquide. Other CO₂-selective membranes that have been commercialized are based on perfluoropolymers and are currently only applied in niche processes (Merkel et al. 2006).

A wide range of other nonporous polymeric membrane materials have been reported in the literature for CO₂ separation, such as polybenzoxazoles, polysulfones, polycarbonates, and polypyrroles (Powell and Qiao 2006). Facilitated transport mechanism selectivity for CO₂ has also been developed, especially for syngas applications. Many of these materials display high CO₂ permeances and CO₂ selectivities relative to other gases present. However, none of these membrane materials have been successfully commercialized to date.

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Carbon Membrane

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Carbon membranes are usually characterized as carbon molecular sieves (CMS membranes) as

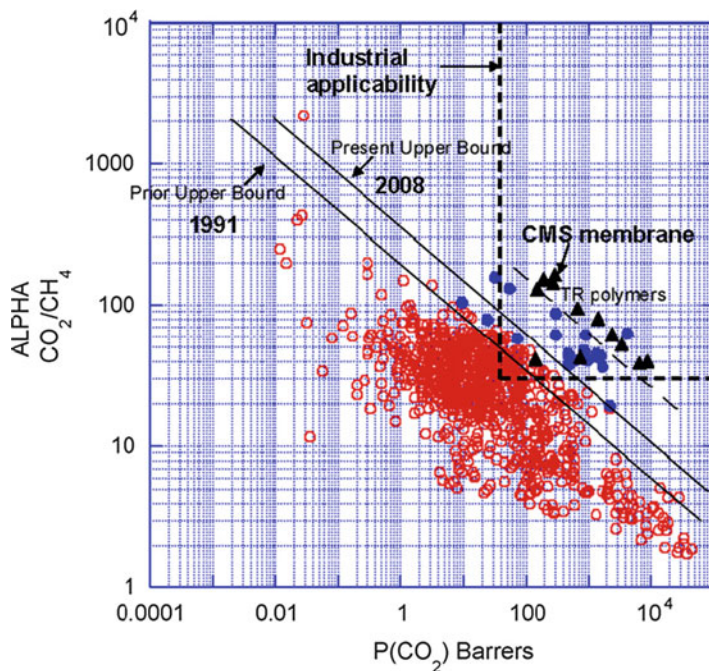
they basically separate based on molecular size. This means that the pores can be tailored for a specific gas mixture, permeating the smallest molecule and retaining the larger ones.

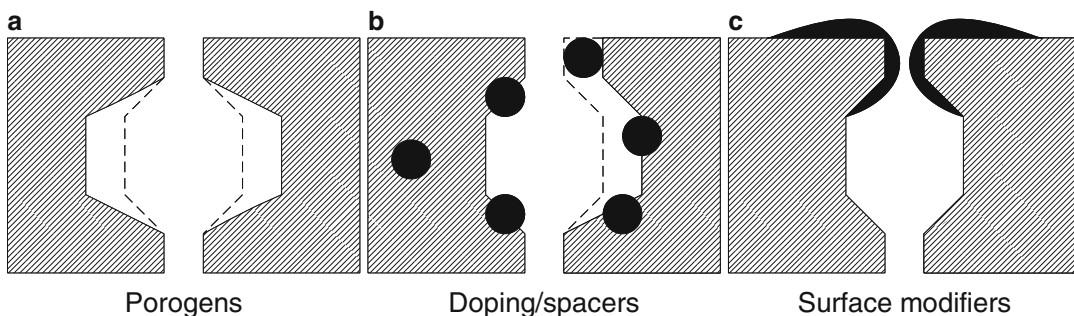
There are two main ways of preparing the CMS membranes: pyrolysis of polymeric hollow fibers or performing pyrolysis of a polymer sprayed onto a ceramic support tube. In both cases a pyrolysis protocol needs to be developed for the specific polymer and pores to be obtained. Important variables to be controlled during the pyrolysis is heating rate, soak time, final carbonization temperature, and which gas to use as purge (typically an inert gas or CO_2) vacuum may also be used. Each of these variables will influence the final pore size and separation properties of the membrane. The final carbonization temperature is usually in the range of 500–900 °C. Carbon membranes are fairly easy to produce on lab scale as much is known on how carbonization conditions affect separation properties (Geiszler and Koros 1996; He and Hägg 2012). However, the scaling up to commercial-size modules may be more of a challenge as commented on further down.

The first carbon membranes were prepared from carbonization of cellulose hollow fibers by Koresh and Soffer (1983). Since then various polymers have been used such as polyimides, polyacrylonitrile (PAN), poly(phenylene oxide) (PPO), cellulose derivatives, and others. The separation properties of CMS membranes are very attractive as their sieving properties easily exceed the upper Robeson boundary of permeability versus selectivity trade-off relationship (Robeson 2008) – this makes it also attractive for industrial applications. The making of the membranes may thus involve six steps: material selection, material functionalization, precursor preparation, pretreatment, carbonization, and possibly posttreatment (Fig. 1). Functionalization usually means adding a porogen or a metal salt to the precursor. The porogen will degrade during the carbonization and thereby increase the pore volume. When the additive is a metal salt (doping the precursor), the final CMS membrane will contain the metal which may functionalize the membrane by showing high affinity to one of the permeating gases (Lie and Hägg 2005). Then if using posttreatment, surface modifiers may adjust

Carbon Membrane,

Fig. 1 Comparing the CO_2/CH_4 Robeson upper bound for dense and thermally rearranged (TR) polymer membranes to the carbon membranes and the region for industrial applicability – data for CMS membranes and industrial applicability region added to the original Robeson plot (see Hägg and He 2011)

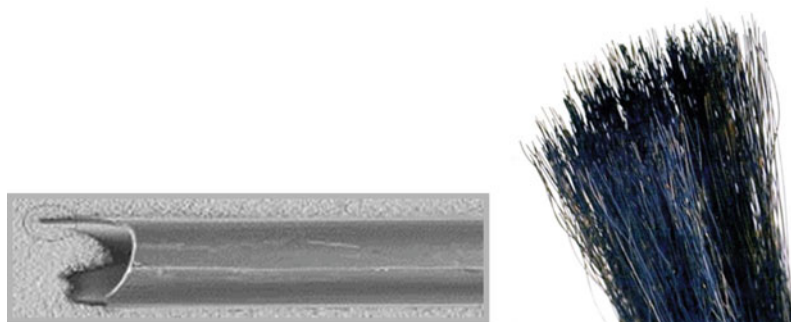




Carbon Membrane, Fig. 2 Schematic model of different ways of tailoring microporous carbon. The *dashed line* shows the limit of an original slit-shaped pore (Lie and Hägg 2005)

Carbon Membrane,

Fig. 3 *Left:* SEM picture of a CMS fiber; wall thickness is 16 μm . *Right:* A bundle of CMS hollow fibers ready for mounting in a pilot module as illustrated by the company MemfoACT in 2013 on their homepage



the pore size. A big advantage of carbon membranes is that they may be used for high-temperature gas separations. This advantage may, however, be compromised if the surface modifier is a degradable polymer at process operation temperature. The different ways of tailoring microporous carbon membranes are illustrated in Fig. 2 (Lie and Hägg 2005).

Although showing excellent separation performance, the self-supported hollow fiber membranes may be quite brittle, thus the scaling up and module making are challenging. The Norwegian company MemfoACT did successfully demonstrate on pilot scale the use of carbonized self-supported cellulose hollow fibers for upgrading of biogas (CO_2/CH_4 separation) (Fig. 3). The scaling up to full-size commercial module has however not yet been reported (in 2015).

The supported carbon membranes will provide better mechanical strength than self-supported fibers but will naturally have lower packing density. These types of carbon membranes have been

especially studied for high-temperature applications (e.g., H_2/CO_2 separation and as carbon membrane reactors). The special challenge of making these membranes is to obtain a defect-free carbon layer on the top of the support – compatibility between support and carbon layer may also be a problem. Supported CMS membranes have been studied by several. A method by using spin-coat technique was developed already in 1996 by Rao and Sirkar (1996). Stainless steel disks (Acharya and Foley 1999) as well as porous α -alumina tubes (Zhou et al. 2003) have been reported as suitable support for pyrolyzed carbon membranes. Acharaya and Foley studied the separation of O_2/N_2 and obtained a separation factor of 12. A challenge of concern with respect to any CMS membrane is the possibility of aging, whereby separation performance may decline over time; hence, the membranes need to be regenerated. Several ways are proposed, such as using heat, purging with air or propane, or using low-voltage direct current at

intervals (Lie and Hägg 2006). The research on CMS membranes is however continuously moving forward, and is well documented, and example is Fu et al. (2015). The main challenge still seems to be scaling up to commercial-size modules.

Potential of Applications

Due to the possibility of tailoring the pores, the CMS membranes have a very nice potential of separating gas pairs which are difficult to separate using other type of membranes and gases which are much alike in structure and physical properties, typically O_2/N_2 and C_3H_8/C_3H_6 (olefin/paraffins in general) (Yoshino et al. 2003). Other type of gas separations can typically be CO_2/CH_4 (both as biogas and as natural gas) and recovery of hydrogen from gas streams such as H_2/CO_2 (precombustion) and H_2 from refinery gasses.

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Carbon Nanotube Membranes (CNT Membranes)

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Carbon nanotubes (CNTs) are allotropic forms of carbon that can be conceptually visualized as a cylindrical nanostructure formed by rolling a graphene sheet along a lattice vectors (m,n) in the graphene plane (Fig. 1).

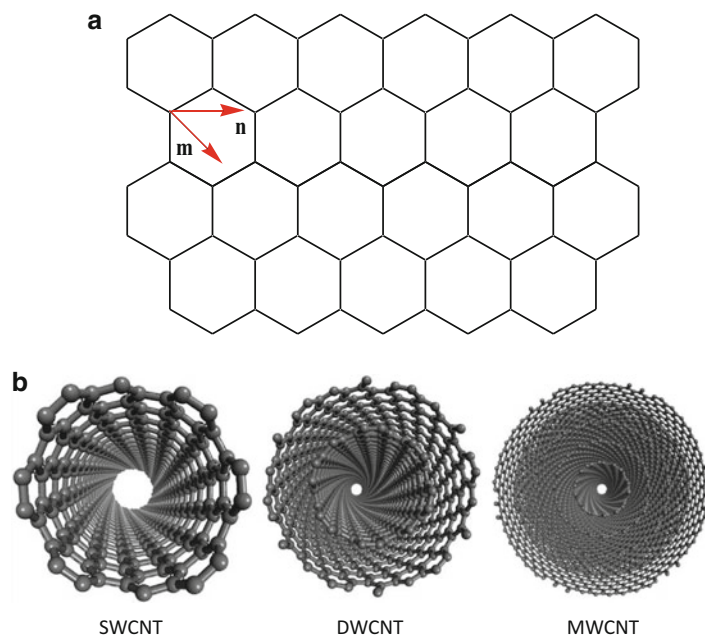
Depending from the number of concentric cylinders, it is possible to have: single-, double-, or multiwalled carbon nanotubes (SWCNTs, DWCNTs, MWCNTs). The indices (m,n) determine the diameter and chirality (i.e., the chiral angle between hexagons and the tube axis) of the CNTs (Dai 2002). The CNTs can be in the zigzag, armchair, or chiral form with metallic or semiconducting properties (Table 1).

CNTs, thanks to their diameter in the nanometer range and their atomically smooth surfaces,

Carbon Nanotube Membranes

(CNT Membranes),

Fig. 1 Schematic honeycomb structure of a graphene sheet (sp^2 hybridized carbon network) (a) and image of single-, double-, and multiwalled carbon nanotubes (SWCNTs, DWCNTs, MWCNTs), (b)



offer unique systems for fast molecular transport (Hummer et al. 2001; Kalra et al. 2003). Molecular dynamics (MD) simulations showed spontaneous and continuous filling of a CNT with a one-dimensionally ordered chain of water molecules.

Membranes made of ordered arrays of carbon nanotubes well aligned along the direction perpendicular to the substrate surface have been already synthesized in which the transport occur through the inner core of the CNTs (Majumder et al. 2011). High permeability enhancement than predictions (>10 for gases and >1000 for liquids) have been obtained with these membranes. However, the small area (typically in the order of few μm^2), the long and complex fabrication process, and the poor mechanical stability of these type of CNT membranes, limit the practical applicability of these interesting nanostructured systems. On the contrary, more easy is the scale up of CNT membranes in which the CNTs are mixed with a polymer in the form of mixed matrix membranes. The main limitations of these membranes are related to the poor dispersion of the CNTs in the polymeric matrix and the moderate increase of the membrane performance.

It is interesting to note that graphitic carbon nanomaterials like CNTs are usually introduced at lower content (≤ 2 wt%) in mixed matrix membranes in comparison with three-dimensional inorganic nanofillers like TiO_2 and ZrO_2 (usually blended at loading ≥ 5 wt%, up to 60 wt%), thank to their high specific surface, elevated aspect ratio, and the intrinsic properties of graphitized structure. In addition, the relatively easy functionalization of the surface of carbon nanomaterials render them ideal candidate to tailor the polymer/nanofiller interface.

CNTs were successfully entrapped in mixed matrix membranes made of various polymeric materials by several techniques including: dispersion in the casting solution and successive phase separation, entrapping in the membrane pores using a polymer binder, in situ crosslinking of a polymer matrix around oriented CNTs (Ismail et al. 2009). The resulting mixed matrix CNT membranes offer, in many cases, relevant advantages in comparison with the polymeric samples. Poly(vinyl alcohol) (PVA)/MWCNTs membranes were realized for pervaporation application, obtaining significant improvement in Young's modulus and thermal stability, as compared to

Carbon Nanotube Membranes (CNT Membranes), Table 1 Different forms of a SWCNT and its electrical properties

(n, m)	Form	Electrical conductivity
(n, 0)	Zigzag 	Metallic when n is multiple of 3, otherwise, semiconducting
(n, m) with n = m	Armchair 	Metallic
(n, m) with m ≠ 0 and n	Chiral 	Metallic when (n-m)/3 is an integer, otherwise, semiconducting

pure PVA membranes (Peng et al. 2007). The entrapment of MWCNTs in polyethersulfone (PES) membranes reduced fouling problems in water treatment (Celik et al. 2011). Mixed matrix membranes consisting of sulfonated carbon nanotubes (sCNTs) and sulfonated poly (ethersulfone ether ketone ketone) (SPESEKK) were also fabricated via the solution casting method (Zhou et al. 2011). The proton conductivity of the SPESEKK membrane increased while the methanol permeability decreased as the sCNTs content increased. MWCNTs were covalently linked to aromatic polyamide (PA) membranes by a polymer grafting process (Shawky et al. 2011). Measurements of mechanical properties

of this composite showed an increased membrane mechanical strength relative to the PA polymeric membranes.

Mixed matrix polyimide membranes were also prepared using functionalized MWCNTs (aminated or oxidized). The MWCNTs functionalization improved their dispersion in the casting solution in comparison to pristine MWCNTs and, as a consequence, in the formed membranes. The membranes containing functionalized MWCNTs showed better performance in the rejection of dyes (enhanced flux and reduced fouling, with similar or higher rejection), with respect to reference polymeric membranes (without MWCNTs). These results were attributed to the formation of low-resistance pathways for solvent transport at the interface between the MWCNTs and the polymeric chains. Moreover, the MWCNTs reduced the severe membrane fouling caused by the absorption of the positively charged dye Safranin (used as a model of organic pollutant) with respect to the polymeric membrane, by a screening effect of the attractive electrical interactions between the Safranin and the membrane surface characterized by a negative value of zeta potential (Grosso et al. 2014).

The presence of oxygen-containing polar groups on oxidized MWCNTs, resulted also in a good dispersion in polyvinylidene difluoride (PVDF) membranes, allowing the formation of mixed matrix membranes with a lower fouling tendency in comparison with the bare polymeric samples (Fontananova et al. 2014).

MWCNTs were also immobilized in the pores of a hydrophobic membrane improving the water-membrane interactions to promote vapor permeability in membrane distillation process (Gethard et al. 2011). In this case, the CNTs dispersion was forced under vacuum into the pores of a polypropylene (PP) membrane, using PVDF as binder.

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Carbon Porous Membranes Modified with Enzymes

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The carbon porous tubes (from Novasep-Orelis-France) have been characterized by average pore diameter of 3 mm and an inner diameter of 0.6 cm (Fig. 1).

The immobilization of enzyme on the carbon tube surface has been carried out by dipping in enzyme solution and then addition of pyrrole monomer just before starting the anodic electropolymerization at +0.9 V vs. Ag/AgCl. The oxidation of pyrrole allowed the entrapment of enzyme in polypyrrole coated on the electrode surface.

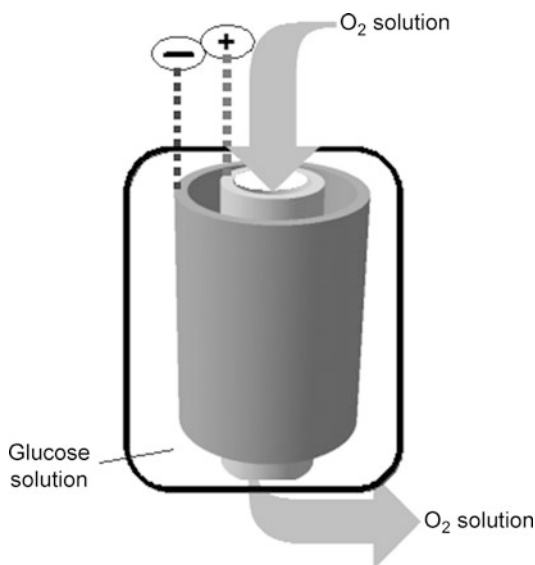
A glucose/O₂ biofuel cell is based on tubular cathode (coated with laccase/ABTS on the external surface for dioxygen reduction) and the tubular anode (coated with glucose oxidase enzyme (GOD) and hydroxyquinoline sulfonic acid as mediator) on the internal surface for glucose oxidation.

The two electrodes were soaked in an unstirred 10 mM glucose solution. Glucose diffused through the polypyrrole film to be oxidized by the GOD at the anode. In order to prevent the presence of dioxygen in the vicinity of GOD, dissolved oxygen was supplied to the system by

Carbon Porous Membranes Modified with Enzymes,

Fig. 1 Photography of carbon tube (photo IEM)





Carbon Porous Membranes Modified with Enzymes,
Fig. 2 Scheme of concentric biofuel cell (thesis of G. MERLE, University Montpellier 2, 2008)

circulating through the inner cavity of the biocathode, then before being reduced at the external surface by the BOD.

Cylindrical and porous carbon tubes were used as original conducting support for the compartment of the bioelectrodes, for enzyme immobilization and transport of dissolved oxygen via diffusive flow through the porosity (Fig. 2). The resulting glucose/oxygen biofuel cell is operated at a maximum power density of 42 mWcm^{-2} at 0.3 V and 37°C in phosphate buffer pH 7.4.

Carman–Kozeny Equation

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Introduction

The Carman–Kozeny equation (or the Kozeny–Carman equation) is a relation to calculate

the pressure drop for laminar flow through a packed bed of solids. It was originally developed by Kozeny in 1927, using the simplified model of a number of parallel capillary tubes of equal length and diameter to describe the packed bed (McCabe et al. 2005). The Kozeny equation is given by

$$\frac{\Delta p}{L} = \frac{KV_o\mu}{\Phi_s^2 D_p^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} \quad (1)$$

where Δp is the pressure drop, L is the total height of the bed, V_o is the superficial or “empty-tower” velocity, μ is the viscosity of the fluid, ε is the porosity of the bed, Φ_s is the sphericity of the particles in the packed bed, D_p is the diameter of the equivalent spherical particle, and K is an empirical constant, which depends on bed tortuosity. The sphericity of a particle is defined by

$$\Phi_s = \frac{6/D_p}{a_v} \quad (2)$$

where a_v is the specific surface area of the particle. If the bed is made of uniform particles, the a_v of the particle represents the specific surface of the bed. The a_v of the particle is simply the surface-volume ratio, i.e., $a_v = s_p/v_p$, where s_p is the surface area of the particle and v_p is the volume of the particle. It follows that for a sphere with the diameter D_p , $a_v = 6/D_p$ and $\Phi_s = 1.0$.

In 1937 Carman applied Eq. 1 to experimental results of flow through packed beds and found that $K = 180$ (Foust et al. 1980). Other references also suggested the value of $K = 150$ (Seader et al. 2011). The Carman–Kozeny equation indicates that the flow is proportional to the pressure drop and inversely proportional to the fluid viscosity. This statement is also known as Darcy’s law, which is often used to describe flow of liquids through porous media.

Extension of the Carman–Kozeny Equation

The Carman–Kozeny equation is applicable for flow through beds at particle Reynolds number (Re_p) up to about 1.0, and

$$\text{Re}_p = \frac{V_o D_p \rho}{\mu} \quad (3)$$

where ρ is the density of fluid. As the flow rate through a packed bed increases, the pressure drop becomes a stronger function of the superficial velocity. At $\text{Re}_p > 1,000$ the pressure drop in packed beds is described by an empirical relation often referred to as the Burke–Plummer equation (McCabe et al. 2005):

$$\frac{\Delta p}{L} = \frac{1.75 \rho V_o^2}{\Phi_s D_p} \frac{1 - \varepsilon}{\varepsilon^3} \quad (4)$$

An equation covering the entire range of flow rates is obtained by assuming that the pressure drop due to viscous losses (Eq. 1) and the pressure drop due to the kinetic energy losses (Eq. 4) are additive. The result is called the Ergun equation (McCabe et al. 2005):

$$\frac{\Delta p}{L} = \frac{K V_o \mu}{\Phi_s^2 D_p^2} \frac{(1 - \varepsilon)^2}{\varepsilon^3} + \frac{1.75 \rho V_o^2}{\Phi_s D_p} \frac{1 - \varepsilon}{\varepsilon^3} \quad (5)$$

The sphericity often does not appear in Eq. 5, which implies the particles in the bed are nearly spherical ($\Phi_s \approx 1$).

Carman–Kozeny Equation in Membrane Processes

The transport of fluid in ► **ultrafiltration (UF)** and ► **microfiltration (MF)** processes is driven by a pressure difference across the membrane (Δp). The UF and MF membranes are porous with the pore size ranges of 2–100 nm and 0.1–10 μm , respectively (Mulder 1996). Because of very small pore sizes, the flow velocity in an idealized straight cylindrical pore of a UF or MF membrane is governed by the Hagen–Poiseuille law (Seader et al. 2011):

$$V = \frac{D^2}{32 \mu L_M} \quad (6)$$

where D is the pore diameter and L_M is the membrane thickness. The mass velocity of fluid (N in

$\text{kg} \times \text{s}^{-1} \times \text{m}^{-2}$) through the membrane is then obtained by multiplying the flow velocity by fluid density and membrane porosity:

$$N = \frac{\varepsilon \rho D^2}{32 \mu L_M} \Delta p \quad (7)$$

In real porous membranes, the pores may not be cylindrical and straight, and Eq. 7 is modified by using the procedure developed by Carman and Kozeny, in which the pore diameter is replaced by the hydraulic diameter (D_H):

$$D_H = \frac{4 A_p}{P} \quad (8)$$

where A_p is the cross-sectional area of the pore and P is the wetted perimeter of the pore. Expressing A_p and P in terms of the specific surface area and the porosity of the membrane leads to an alternative expression for D_H (Seader et al. 2011):

$$D_H = \frac{4 \varepsilon}{a_v (1 - \varepsilon)} \quad (9)$$

The actual pore length is longer than the membrane thickness and can be represented by τL_M , where τ is a tortuosity factor > 1 . Substituting Eq. 9 and the tortuosity factor into Eq. 7 gives

$$N = \frac{\varepsilon^3 \rho}{2(1 - \varepsilon)^2 a_v^2 \mu \tau L_M} \Delta p \quad (10)$$

Equation 10 is an alternative representation of the Carman–Kozeny equation. Recognizing that $\Phi_s D_p = 6/a_v$, the actual fluid velocity in the bed $V = V_o/\varepsilon$, replacing L by L_M , and multiplying by the fluid density ρ , Eq. 1 can be rearranged to

$$N = \frac{\varepsilon^3 \rho}{(K/36)(1 - \varepsilon)^2 a_v^2 \mu L_M} \Delta p \quad (11)$$

If $K = 150$, the comparison of Eq. 10 with Eq. 11 leads to $\tau = 2.08$; on the other hand, with $K = 180$ $\tau = 2.5$. In other words, the numerical

value of the empirical constant in the Carman–Kozeny equation depends on the tortuosity of the packed bed, which in general ranges from 2.0 to 2.5. In the case of the porous membranes, the tortuosity can be greater than that of the packed bed.

The porosity and the specific surface area of porous membrane can be determined experimentally. If the membrane tortuosity along the membrane thickness is known, Eq. 10 allows to predict the mass velocity of fluid through the membrane under a given pressure gradient across the membrane. Alternatively, for a given mass fluid velocity, Eq. 10 can be used to predict the required pressure gradient across the membrane.

The mass velocity of fluid through the membrane can also be expressed in terms of bulk-flow permeability (P_M), which is a measure of the membrane productivity (Seader et al. 2011):

$$N = \frac{P_M}{L_M} \Delta p \quad (12)$$

It follows from the comparison of Eq. 10 with Eq. 12 that the bulk-flow permeability in porous UF and MF membranes is given by

$$P_M = \frac{\varepsilon^3 \rho}{2(1 - \varepsilon)^2 a_v^2 \mu \tau} \quad (13)$$

The rearranged form of the original Carman–Kozeny equation given by Eq. 11 can be used to predict the bulk-flow permeability of microfiltration membranes prepared by sintering. This method of membrane formation involves compressing a powder consisting of particles of a given size and sintering at elevated temperatures (Mulder 1996). Consequently, the final membrane has a structure similar to that of the packed bed.

The Carman–Kozeny equation is also applicable for the analysis of membrane processes in which the transport of fluid through the membrane is associated with cake formation on the membrane surface (Mulder 1996). In this case, the fluid which permeates through the membrane must overcome two resistances in series, the resistance to flow through the cake (R_C) and the

resistance to the flow through the membrane (R_M). Consequently, the expression for the mass velocity of fluid can be written as follows:

$$N = \frac{\Delta p}{\mu(R_C + R_M)} \quad (14)$$

and

$$R_C = \left(\frac{K}{36} \right) \frac{(1 - \varepsilon)^2 a_v^2 \mu L_C}{\varepsilon^3 \rho} \quad (15)$$

$$R_M = \frac{2(1 - \varepsilon)^2 a_v^2 \mu \tau L_M}{\varepsilon^3 \rho} \quad (16)$$

If there is no adsorption of solute particles inside the membrane pores, R_M is constant, but since the cake thickness (L_C) increases with the amount of feed processed through the membrane, R_C increases accordingly. Equations 14, 15, and 16 are analogous to those used to describe the conventional cake filtration.

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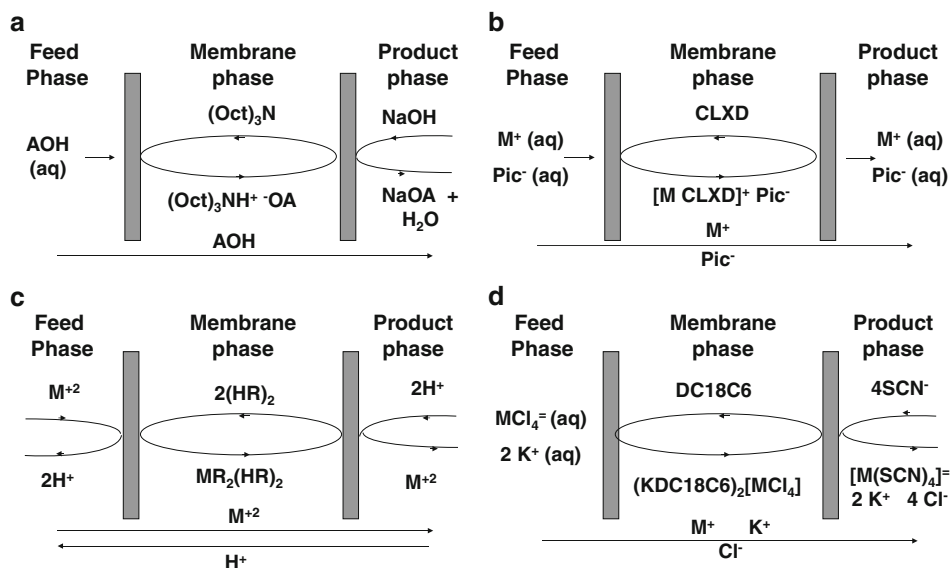
Carrier-Mediated Transport

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Transport mechanism used to improve flux, permeability, and selectivity in membrane separations. It is also known as type 2 facilitated

transport or carrier-facilitated transport (Ho and Li 1992). A carrier reagent is incorporated in the membrane phase to transfer the diffusing specie from the feed phase to the product phase across the membrane phase. Although fixed carriers (bonded within the membrane solid matrix either by electrostatic forces or by covalent linkages) have been described, liquid membranes employ mobile carriers, i.e., compounds (soluble in the membrane phase but insoluble in the feed and the product phases) which are added to the membrane phase to form with the specie to be separated into a reversible compound or complex, soluble in the membrane. This compound is formed in the interface feed phase/membrane phase, it is transported through the membrane phase due to its concentration gradient, and it is broken in the membrane phase/product phase interface. Then, the specie to be separated is liberated in the product phase, and the carrier diffuses in the contrary way through the membrane phase, as a consequence of its concentration gradient, to the opposite interface, to initiate a new separation cycle. So, the transport of the target species can be broken down to the following steps: (1) diffusion of the target specie from

the bulk feed phase across the aqueous boundary layer to the feed phase/membrane phase interface; (2) formation of carrier-target specie compound; (3) diffusion of the carrier-target specie compound across the membrane; (4) breakage of the carrier-target specie compound at the membrane phase/product phase interface, releasing both the target specie and the carrier; (5) diffusion of the released target specie from the membrane phase-product phase interface to the bulk strip phase; (6) return of the released carrier across the membrane to the feed phase/membrane phase interface (Marr and Knopp 1982). In this way, each carrier molecule is able to transport solute molecules as many times as necessary, so that only a small amount of the carrier is required in the membrane phase even for achieving a high degree of separation. As the process ends when the concentration of the specie to be separated equalizes on both sides of the membrane, carrier-mediated transport can be improved by incorporating a chemical reaction on the receiving side in two ways. The first is by reducing the concentration of the specie to be separated to practically zero on the product side through an auxiliary reaction in the product phase,



Carrier-Mediated Transport, Fig. 1 (a) Carrier-mediated transport of an acid with tri-n-octylamine, (b) carrier-mediated co-transport of a metallic ion and its accompanying anion with a calixarene derivative

(CLXD), (c) carrier-mediated counter-transport of a metallic ion by an organophosphorus carrier (HR)₂, and (d) carrier-mediated co-transport of a metallic ion and accompanying anion and cation with a crown ether (DC18C6)

to form a compound insoluble in the membrane and release the carrier to begin a new separation cycle. The second is by maintaining the driving force for the transport of the target specie through maintaining a concentration gradient of a second specie transported in the opposite direction. Carrier-mediated transport combines the process of extraction and stripping in a single unit operation, and it offers the possibility of transporting a component against its own concentration gradient (Ho and Li 1992; Kislik 2010). In carrier-mediated transport, two different species can be transported at the same time, giving a coupled transport, in which the membrane contains a carrier which can only lead to transport when two different species present themselves at the same time. If the transport of the two species occurs in the same direction (from the feed to the product phase), we can speak of co-transport. On the other hand, if it occurs in opposite directions (one is transported from the feed to the product phase and the other from the product to the feed phase), we can speak of counter-transport. Different examples of carrier-mediated transport are shown in Fig. 1.

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Cascade Diafiltration

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Cascade systems may be used when the product is in the permeate of a microfiltration or ultrafiltration system.

Consider a two-stage cascade. Constant volume diafiltration is performed in the first stage to maximize the recovery of the product which passes through the membrane. The product-containing permeate enters the second stage where it undergoes batch ultrafiltration using a membrane which retains the product.

Cascades can be operated in open-loop or closed-loop configurations (Charcosset 2012). In the open-loop configuration, the permeate from the second stage goes to drain. In the closed-loop configuration, the permeate from the second stage is used as the diluant for the first stage, thus reducing substantially the volume of fresh diluant required.

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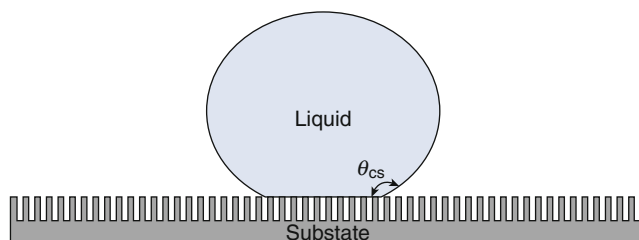
Cassie–Baxter Model

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The Wenzel regime is usually recognized as homogeneous wetting, since the liquid completely penetrates into the grooves. While under some circumstances, especially the increase of the surface roughness, vapor pockets may be trapped underneath the liquid yielding a composite interface. This heterogeneous wetting is usually described by the Cassie–Baxter (CB) model, from which the apparent contact angle (θ_{CB}) is given by equation: (Cassie and Baxter 1944)

$$\cos \theta_{CB} = f_s \cos \theta_c + f_v \cos \theta_v \quad (1)$$

where θ_c is the intrinsic contact angle on the original smooth surface and f_s and f_v are the area



Cassie–Baxter Model, Fig. 1 Vapor pockets are trapped between the grooves and the liquid droplet. This state is essential for superhydrophobicity and is described by

Cassie-Baxter model (Hsu et al. 2011, reproduced with permission from Elsevier Ltd.)

fractions of the solid and vapor on the surface, respectively. Since $f_s + f_v = 1$ and $\theta_v = 180^\circ$ (implying that a suspended liquid droplet in air is a perfect sphere), Eq. 1 can be rewritten as follows:

$$\cos \theta_{CB} = f_s (\cos \theta_c + 1) - 1 \quad (2)$$

From Eq. 2, it can be found that droplets will have a higher apparent contact angle if less area is in contact with the solid substrate. The CB equation simply indicates the contact angle can be increased even when the intrinsic contact angle of a liquid on the original smooth surface is less than 90° .

New developments in the field show that there may need to be taken other considerations for contact angles and contact angle hysteresis. It is suggested that the contact line model is a better approach to predict the superhydrophobicity of surfaces (Gao and McCarthy 2007, 2009) (Fig. 1).

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Casting

Francesco Galiano

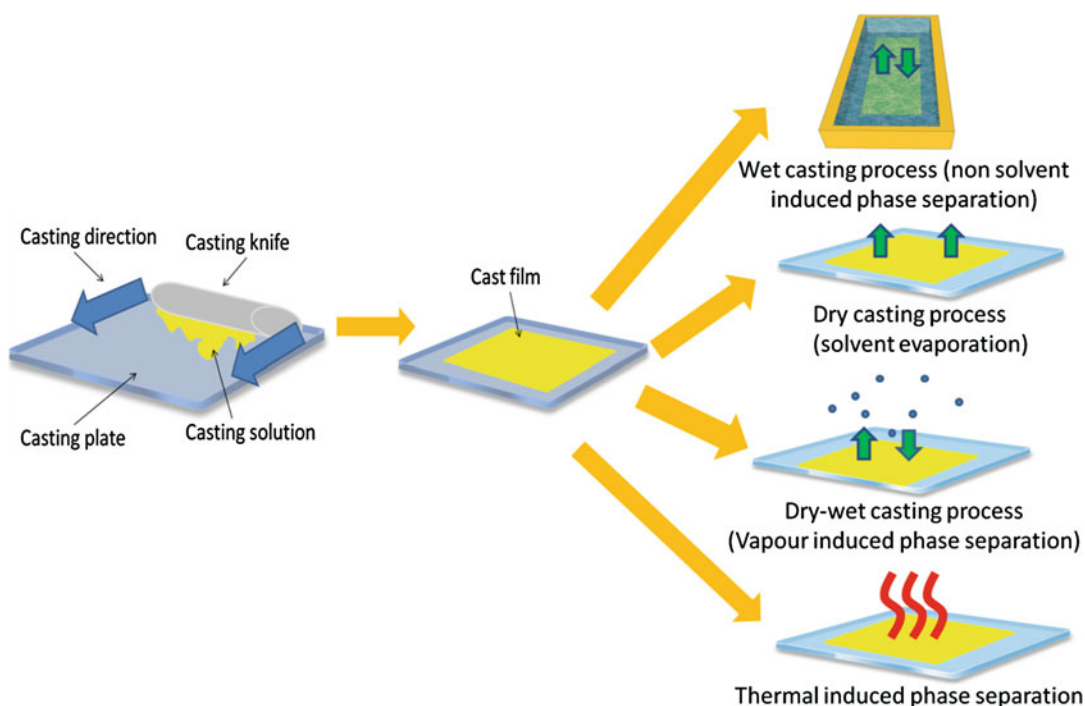
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Casting is the main technique applied for the preparation of flat polymeric membranes using phase inversion process (such as NIPS, VIPS, etc.). The procedure for casting flat sheet membranes can be summarized as follows:

1. Preparing the casting solution by dissolving the polymer in the appropriate solvent
2. Placing a suitable casting plate (a belt, a glass, or other supports)
3. Adjusting the desired casting knife thickness
4. Pouring the polymeric solution on the casting plate
5. Uniformly spreading out the polymeric solution across the casting plate (Fig. 1)

Then, based on the way the phase separation occurs, the following techniques can be distinguished:

- Wet-casting process: the cast film is immersed into a coagulation bath, and due to solvent/nonsolvent exchange, the precipitation of the polymer occurs.
- Dry-casting process: the volatile solvent is left to evaporate from the cast film leading to the precipitation of the polymer.



Casting, Fig. 1 Procedure for casting flat sheet membranes at lab scale and methods for inducing phase separation

- Dry-wet-casting process: the cast film is exposed to a nonsolvent vapor (generally water) for a fixed time and then immersed into a coagulation bath.
- Thermal-induced phase separation: the cast polymer solution prepared at elevated temperature is cooled down causing phase separation and polymer precipitation (Drioli and Giorno 2009).

Manual and automatic casting machines are used both at laboratory and at industrial scale. In the latter case, the casting machine is on purpose created for specific applications. Commercial membranes are, usually, cast on porous supports made up, for instance, of a nonwoven polyester material in order to improve their mechanical stability, obtaining composite membranes.

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Casting Solution

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Casting solution is used to prepare membranes by casting method. Polymer and solvent are the main components of the solution system, but various additives can be also added. The choice of the polymer is of primary importance in preparing the casting solution. The polymer, in fact, must be soluble in the selected solvent in an appropriate concentration which is strictly related to final membrane application. Low concentrations of polymer, in fact, generally lead to a membrane with a porous structure, while high concentrations of polymer produce membranes with a more dense structure. The typical solution casting, with a polymer concentration ranging from 15 to

20 wt.%, is used for the preparation of porous ultrafiltration membranes. On the contrary, a solution casting containing higher concentrations of polymer, up to 25 wt.%, is used for the preparation of reverse osmosis, gas separation, and pervaporation membranes.

Even the choice of the solvent is not arbitrary but based on specific requirements. The solvent must dissolve the polymer, and it must be miscible with a nonsolvent, when it is used as coagulation medium, taking into account both kinetic and thermodynamic aspects. Due to the fast demixing in water, aprotic solvents, such as dimethyl formamide, dimethyl acetamide, or dimethyl sulfoxide, are preferred if membranes with a porous and asymmetric structures have to be obtained. On the contrary, solvents causing a slow precipitation of the polymer, such as acetone or tetrahydrofuran, are used for the production of dense membranes.

Addition of various modifiers in the solution casting allows to adjust membrane properties on the basis of final membrane application. Cosolvents, nonsolvents, and fillers of different types, such as pore forming and cross-linking agents, can be added to the casting solution (Drioli and Giorno 2009). Although these additives are used in low concentrations, they are determinant for the final membrane performances and applications.

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Casting Solution Additives

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A casting solution is normally prepared to be filmed as a flat sheet, or extruded as a hollow

fiber, in polymeric membrane preparation via phase inversion. The two main components of a casting solution are the selected polymer (P) and a suitable solvent (S) (or a diluent, for membrane preparation via TIPS). Different types of additives can be introduced in the casting solution composition to improve/enhance some selected membrane properties, depending on the application. Additives can be divided in two categories: soluble and insoluble additives. Soluble additives can be, in general, salts, as LiCl and LiClO₄; small molecules, as glycerol or ethylene glycol (EG); or polymers, as polyethylene glycol (PEG) or polyvinyl pyrrolidone (PVP), with different molecular weights (Mw). Most soluble additives are introduced to enhance the formation of membrane pores and are called “pore former” or “pore forming.” They are normally leached out from the membrane matrix in the coagulation bath. However, high Mw additives, as PVP, can be retained in the membrane structure. This effect can be exploited to tailor membrane wettability, since PVP is hydrophilic. Similarly, a class of poly(ethylene oxide)-b-poly(propylene oxide)-bpoly(ethylene oxide) triblock copolymers, referred to as Pluronic[®], can be used as additives to improve membrane hydrophilicity, thanks to their stable incorporation in the polymeric matrix. The effect of soluble additives on the membrane morphology depends on a trade-off between thermodynamic and kinetic factors. Soluble additives can increase the thermodynamic instability of the casting solution. This can be detected from a shift of the binodal curve toward the P/S axis, in ternary phase diagrams, which indicates less non-solvent (NS) tolerance of the P/S/Additive system, with respect to the P/S system having the same polymer concentration. This normally promotes phase inversion, resulting in more porous structures, and may enhance macrovoids formation as well. However, additives can also increase the dope viscosity. This will hinder the S/NS exchange and, hence, delay phase inversion. As a result, membrane structure can shift to more spongy type, while macrovoids formation may be reduced. For instance, PVP affects both the thermodynamic and kinetic of the phase-inversion process due to its hydrophilicity and

its effect on the dope viscosity (Simone et al. 2010). Hence, the effect of PVP on the final membrane morphology and properties depends both on its concentration and molecular weight. On the one hand, PVP concentration is directly connected with the thermodynamic of the P/S/Additive/NS system. On the other hand, the casting solution viscosity increases with polymer concentration and molecular weight. Finally, the additive leaching from the polymeric matrix is more difficult as its Mw increases. Several examples of casting solution soluble additives effect on membrane morphology and properties can be found in literature. For instance, the analysis of PVP effect on the kinetic and thermodynamic of phase inversion during preparation of polysulfone (PS) membranes was carried out by Lee et al. (2003). Mansourizadeh et al. (2010) found that lithium chloride acted as a phase-inversion promoter additive and was leached out in the coagulation bath in the preparation of poly(vinylidene fluoride) (PVDF) hollow fiber membranes. This resulted in fibers with reduced pore size, high surface porosity, and low mass transfer resistance.

Susanto et al. (2009) reported that Pluronic[®] improved the wettability of polyethersulfone (PES) membranes, thanks to its amphiphilic, surfactant properties, and was stably integrated in the membrane matrix. Other relevant examples for each additive type can be found in the review by Guillen et al. (2011).

Insoluble additives can be also used to tailor certain membrane properties. Inorganic fillers, as zeolites, metal oxides (as TiO₂, ZnO, Al₂O₃), hydrophobic/hydrophilic cloisite, and carbon-based fillers (graphene oxide, nanotubes, fullerenes), can be incorporated, usually as powders of nanometric size, in the casting solution, for preparing mixed-matrix membranes (MMM). In this case, filler stability in the membrane matrix, as well as its uniform dispersion, is among the key issues. For example, TiO₂ nanoparticles (NPs) show photocatalytic, antibacterial, antifouling, and UV-cleaning properties. They can be introduced in the membrane matrix to enhance

wettability and endow membranes with self-cleaning, antifouling, and antibacterial properties (see, for instance, the work by Song et al. 2012). Zeolites and carbon-based fillers can be used to overcome the typical trade-off between membrane productivity and selectivity in different applications, as gas separation and pervaporation (see Clarizia et al. 2004; Vu et al. 2003; Dobrak et al. 2010). Other insoluble additives, as silica particles, can be etched out, using proper acid/alkaline treatment, and work as pore formers (Hashim et al. 2011).

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Catalyst Entrapment

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Catalyst entrapment refers in a membrane context to the confinement of a catalyst in a membrane. The catalyst can be either a homogeneous or heterogeneous catalyst, or an enzyme. Two basic ways exist for the entrapment. In the first approach, the (bio)catalyst is dispersed or dissolved in the polymer solution, which after forming into a flat-sheet or hollow-fiber membrane can be turned into a dense or porous catalytic membrane. If of a porous nature, the pore sizes should obviously be smaller than the (bio)catalyst to prevent leaching. If of a dense nature, steric occlusion can also help to retain the catalyst inside the polymer, but this will also happen when the affinity for the polymer matrix is much higher than for the reaction mixture, hence prohibiting catalyst dissolution in the contacting reaction fluid (Vankelecom 2002). In the second approach, encapsulation can be applied (McMorn and Hutchings 2004). Confinement of a liquid which contains the (bio)catalyst is then taking place within small capsules enclosed by a polymer or a surfactant.

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Catalyst Immobilization in Membranes

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By incorporating catalysts in membranes, a new environment is created around the catalyst which can in several ways influence the catalytic activity and selectivity of the catalyst. The membrane can block certain inhibiting compounds from the catalyst surroundings by steric exclusion or by decreasing the sorption tendency of that compound and/or its diffusion to the catalyst. Alternatively, it can facilitate the transport of desired compounds to the reactive sites. When incorporated in a membrane, other reactor setups can become available, e.g., with the two reagents contacting the membrane (and thus the immobilized catalyst) from the different sides.

Different methodologies exist to immobilize homogeneous catalysts in membranes: via a covalent or coordinative bond between the catalyst and the membrane, via electrostatic interactions between them, through steric occlusion of the catalyst in a matrix or through physical adsorption of the catalyst on the membrane surface or in its pores. For homogeneous catalysts in specific, extra advantages appear upon immobilization in a membrane. This can be in fact a strategy to heterogenize the catalyst; it allows good dispersion of the homogeneous catalyst into the reaction environment and finally also offers an easy way for reuse. Additives that boost the catalyst performance can also be co-immobilized. On the other hand, leaching of the catalyst or these additives from the membrane can be a problem under certain liquid-phase reaction conditions.

When heterogeneous catalysts are immobilized in polymeric membranes, this is most commonly done by dispersing them in

the membrane casting solution. Key is then to find a good solvent for the polymer that initially allows creation of a good dispersion of the heterogeneous catalyst and that is subsequently evaporated fast enough to avoid settling of the catalyst particles, leaving an even membrane behind.

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Catalyst Loading

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The term “catalyst loading” refers to the amount of catalyst present in a catalytic membrane, most commonly expressed as mol/g or g/g.

If the catalyst is incorporated in the membrane already during the membrane preparation (in contrast to a post-synthesis catalyst deposition), dispersion problems can appear, especially at higher loadings. This can be reflected in aggregate formation for heterogeneous catalysts and in cluster formation or even precipitation for homogeneous catalysts. When the catalyst is present during membrane preparation, side effects might complicate the preparation of the catalytic membrane, such as interference of the catalyst with the solvent evaporation or the polymer curing or settling of the catalyst.

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Catalyst Retention by Membranes

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When coupling catalysis to membrane separations, the catalyst retention expresses in general the amount of catalyst that does not pass the membrane while filtering the reaction mixture over a membrane. Such mixture can either contain a homogeneous or heterogeneous catalyst. The membrane used to retain it will then need to have a pore size able to retain the dissolved/dispersed catalyst by size. If dense membrane is applied, good retention can also be realized by lowering the affinity of the membrane material for the catalyst or the diffusion of the catalyst through it. The filtration can be driven by a variety of driving forces (pressure, concentration, electrical, thermal), depending on the reaction type that is run and the conditions under which the reaction is taking place. The separation can run at the same time as the reaction in a continuous hybrid process, or the removal of the catalyst can take place batchwise. In the latter case, the conditions for the separation can be different from the conditions during reactions; hence, both can be optimized separately (Vankelecom 2002).

Retention and rejection by a membrane refer to the same effect of withholding a compound by a membrane, but by definition, retention refers to a concentration of the removed compound in the feed, while rejection refers to the concentration in the retentate (Mulder 1991). In continuous processes or when using large feed volumes from which only small quantities are filtered, both definitions become equal.

Many of such membrane-assisted catalytic reactions have been described, where the membrane separation process is either pervaporation (very popular to shift the equilibrium of the reaction to the right by removing the products of the

reaction), vapor permeation, gas separation, ultrafiltration (solvent resistant), nanofiltration, reverse osmosis, or dialysis. They all aim at an easy recovery of the catalyst or at operating in continuous or semi-batch mode. A very high catalyst retention is required, since the continuous loss of small amounts of catalyst adds up seriously after treating several batches or in a long-term continuous process (Brinkmann et al. 1999). Tricks to increase the catalyst retention can be to enlarge the catalyst by creating polymeric, dendrimeric, or hyperbranched versions of the homogeneous catalysts (Van Koten et al. 2002; Muller et al. 2005).

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Catalytic (Pt-Y) Membranes

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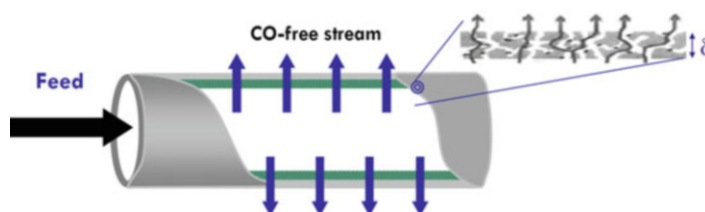
Today, about the 60–70 % of hydrogen is produced by steam reforming. The reaction products

are a mixture of CO and H₂. Additional hydrogen can be recovered by a lower-temperature gas-shift reaction. At the end of this process, the amount of carbon monoxide is equal to 1 %. This CO amount is not tolerated by the PEM fuel cells. In order to avoid cell performance degradation, carbon monoxide concentration must be kept below 10 ppm in the hydrogen feed streams (Rohland and Plzak 1999); CO selective oxidation (selox) is an interesting and economic approach for a deep purification of H₂-rich gas streams from carbon monoxide (Avgouropoulos and Ioannides 2003). During this process two competitive reactions take place, carbon monoxide and hydrogen oxidation, and so a selective catalyst is required to avoid hydrogen consumption. Among the various catalysts used, the better is the platinum because it represents a good compromise between cost and performance. It demonstrated the possibility to use Pt-Y membranes as innovative devices to perform the CO selective oxidation (Hasegawa et al. 2002). These systems permit to disperse catalytic nano-sized particles in a thin zeolite layer assuring a good contact between reactants and catalytic sites and at the same time a low pressure drop and reduced bypass (Fig. 1).

Catalytic zeolite membrane Pt-loaded demonstrated the possibility to reduce the CO concentration from 10,000 ppm down to 10–50 ppm (Bernardo et al. 2006, 2008). The membrane with the best permeation properties exhibited the best catalytic performance (amount of CO at the outlet stream equal to 10 ppm). A negligible effect of the feed pressure was obtained with the low-permeance membranes. On the contrary,

Catalytic (Pt-Y) Membranes,

Fig. 1 Scheme of a catalytic zeolite membrane reactor



positive effect was found by using more permeable membranes. The effect of the pressure on CO conversion can be explained considering two different paths for the reactants: through the zeolite channels (first path) and defects (second path). CO molecules permeating into the zeolite channels interact with the catalyst (Pt) with very high probability owing to the narrow space of the zeolite pores. In this case, the effect of pressure is negligible on the conversion. On the contrary, the interaction of the CO molecules with the catalyst depends on the pressure owing to the large volume of the support pores.

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- aluminum (Szostak 1998). The resulting structure is very regular with pore size at molecular scale. Their adsorption properties change varying the Si/Al ratio during the synthesis because it determines the number of cations in the structure and so their hydrophilicity (Szostak 1998). When the cation is a proton, a Brønsted acid site is formed in the zeolite structure (Abott and Guerzoni 1992). In addition, different transition metals can be loaded (by cationic exchange) into the zeolite channels (Howe 2004). These inorganic crystals are used at industrial level as adsorbents for the purification and separation of different substances and as exchangers in laundry detergents (Smulders et al. 2003). Furthermore, they are largely used as catalysts (Weitkamp 2000). In catalysis, the best performances of the zeolite with respect to the other systems are the high concentration of acid sites and their high thermal and hydrothermal stability. Besides, their shape selectivity plays a very important role to orient the reaction toward the production of the desired product (Chen et al. 1989). They are used in different acid-catalyzed hydrocarbon transformations such as cracking, isomerization, and alkylation which are very important reactions in the petrochemical industry, and increasing attention is also focused in environmental catalysis and synthesis of fine chemicals (Xu et al. 2006). The oldest and largest application of the catalytic zeolites in oil refining is the fluid catalytic cracking (Martinez and Corma 2011). Hydrocracking is the second largest application of zeolite in this field. In this last process, zeolites are used for their high stability toward the deactivation by coking or by nitrogen compounds (Ward 1993). In the petrochemical process, very relevant is the production of the most important isomer of the xylene (para-xylene) because it is used for the production of terephthalic acid that in turn is used for the synthesis of polyester resin and fibers. This process is carried out by using ZSM-5 zeolite taking advantage of its shape selectivity property and low coking tendency (Corma et al. 2011). A further development of zeolite chemistry (e.g., synthesis of structures with more large pores) will open new possibilities for processes in chemical, fine chemical, and biomass transformations.

Catalytic Crystals

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Zeolites are crystalline microporous materials. They are composed of AlO₄⁵⁻ and SiO₄⁴⁻ tetrahedra that build a network of channels and cavities. Extra-framework ions are located in the pores and cavity to balance the negative charge of the

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Catalytic Diffuser

- [Contactor-Type Catalytic Membrane Reactor](#)

Catalytic Membrane Bioreactors with Biocatalysts Segregated Within the Pores of Asymmetric Membranes

- [Biocatalytic Membrane Reactors \(BMR\) with Biocatalysts Entrapped Within the Pores of Asymmetric Membranes](#)

Catalytic Membrane Reactors with Biocatalysts Segregated Within the Pores of Asymmetric Membranes

- [Biocatalytic Membrane Reactors \(BMR\) with Biocatalysts Entrapped Within the Pores of Asymmetric Membranes](#)

Catalytic Membranes

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A catalytic membrane is a membrane with catalytic properties. The catalytic activity can be intrinsic to the material itself, as in the case of membranes made of Pd, TiO₂, and H-ZSM-5 zeolite, which are catalytic for specific reactions, or can be obtained by coating the external or the internal (porous) surfaces of the membrane with the catalyst (metal or oxides) or even by occluding the catalyst (metal nanoclusters, zeolites, activated carbon, metal complexes) inside a dense polymer matrix (Gryaznov 1986, 1992; Irusta et al. 1998; Gobina and Hughes 1994; Saracco and Specchia 2000; Itoh 2000; Dittmeyer et al. 2001; Piera et al. 2001; Julbe 2005; van Dyk et al. 2003; Marcano and Tsotsis 2002; Basile 2012; Fritsch and Peinemann 1995).

Catalytic membranes can be inorganic (metallic, ceramic, or carbon made) or polymeric in their nature. Examples of dense inorganic catalytic membranes are the ones made of palladium, which are catalytically active for hydrogenation reactions (though presenting low activity), while porous catalytic inorganic membranes can be made of a variety of materials, namely, alumina, silica, titania, and zeolites among others. Porous polymeric membranes are usually made, for example, of polysulfone, polyacrylonitrile, or polypropylene, while dense polymeric membranes are prepared from PDMS (polydimethylsiloxane) and other silicones, PVA (polyvinyl alcohol), perfluoropolymers, polyimides, or polyamides among other polymers (Basile and Gallucci 2011; Basile 2012).

Membranes in general can be permselective or nonpermselective. Catalytic permselective membranes are characterized by two important parameters concerning their separation ability: Permselectivity, which describes the ability of the membrane to transport the different components of a mixture at different rates, and the permeability, which quantifies the total amount permeated by the membrane when subjected to specific operation conditions. Nonpermselective membranes can be described by their permeability, but they are not able to discriminate between the different components of a mixture (Marcano and Tsotsis 2002).

The mass transport mechanism suitable to describe the permeation rate through a (catalytic) membrane is primarily a function of the type of membrane. For dense membranes, the accepted model is the sorption (solution) diffusion (the permeant species in gas or liquid phase sorbs into the membrane at the higher chemical potential side, diffuses through the membrane subjected to the driving force gradient, and desorbs on the opposite side). These membranes are usually permselective. Concerning porous membranes, the total mass transport results from different contributions, namely, a diffusive component (activated, surface, Knudsen and bulk) and a viscous component (Poiseuille flow). The contribution of each one depends on the operating conditions and on the pore's size. For pore radius between 1 and 50 nm, Knudsen diffusion is normally the predominant mass transfer mechanism (Knudsen diffusion is characterized by the mean-free path of the traveling species being much larger than the pore radius and is independent of any pressure gradient along the pore), and the membranes present some permselectivity, related with the ratio of the species molar mass. For membranes with larger pores, namely, macroporous, the mass transfer mechanism is a viscous flow if a total pressure gradient across the porous membrane is present or bulk diffusion if not. Neither of these situations allows any permselectivity. When the membrane has micropores and the species adsorb significantly, as in

the case of zeolites, surface diffusion has a relevant contribution. Also in these cases the membranes are permselective (Basile and Nunes 2011).

A catalytic membrane is used to carry out different types of reactions, namely, chemical, biochemical, electrochemical, or photocatalytic, in a so-called membrane reactor. The type of membrane to be used, porous or dense, polymeric or inorganic, etc., depends on several factors, namely, the type of reaction. For example, dense polymeric catalytic membranes are used for low-temperature reactions where the permselectivity is important for shifting the conversion beyond the thermodynamic equilibrium value based on feed conditions (e.g., selective removal of water in esterification reactions) or to enhance the reaction selectivity (e.g., hydration, epoxidation, isomerization, and hydrogenation reactions). Dense polymeric catalytic membranes can also be used as contactors for promoting reactions between two immiscible phases with segregated feed (e.g., oxyfunctionalization of hydrocarbons with hydrogen peroxide reactions) (Basile and Gallucci 2009).

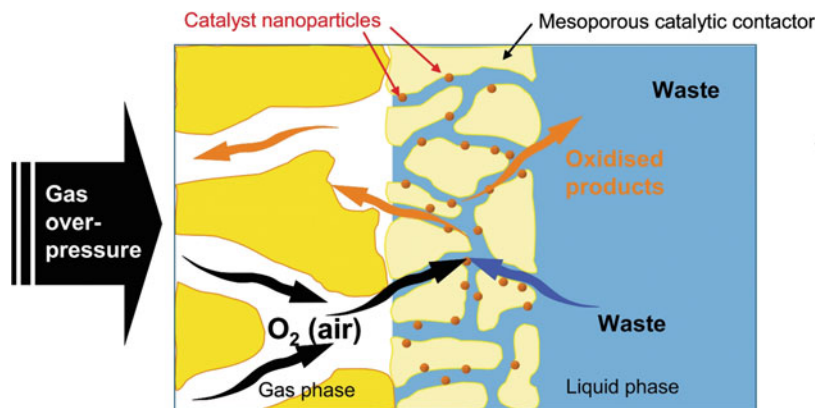
Another type of reaction that has been studied is the photocatalytic removal of contaminants from water, either using porous or dense polymeric catalytic membranes. The catalyst typically used is TiO_2 , occluded or coated, but also occluded Fe in an H_2O_2 oxidant medium (photo-Fenton process) has been considered (Basile and Nunes 2011).

Catalytic nonpermselective porous membranes, polymeric or inorganic, can be used to improve the contact between the reactants and the catalyst, in order to obtain higher reaction conversions. Particularly in the case of triphasic (gas/liquid/solid) reactions, usually limited by the diffusion of the gaseous reactant, porous membrane reactors show conversion advantages. By controlling the pressure of the gas and liquid flows, it is possible to shift the reactants to meet the catalyst zone (Fig. 1).

The same segregated feeding strategy can also be used in cases of reactions where a strict control

Catalytic Membranes,

Fig. 1 Porous catalytic membrane for wastewater treatment (Reprinted with permission from Raeder 2010)



of the reactants is important, namely, in the case of very fast or highly exothermic reactions. In the case of reactions where a complete conversion of some components, like VOCs, is of high importance, porous catalytic membranes, permselective or not, are usually used in a “flow-through” mode, that is, all the reactants are fed conjointly. In these cases, it is critical controlling the residence time of the reactants to guarantee a complete conversion (Westermann and Melin 2009).

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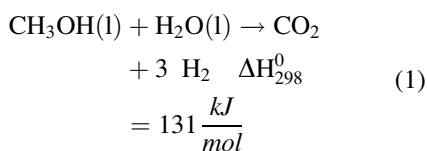
Catalytic Methanol Steam Reforming

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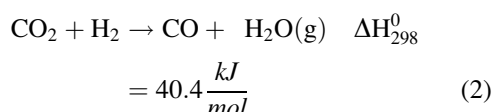
Methanol receives increasing interest as future energy carrier for distributed and mobile power generation, because it can be produced via sustainable routes and has a high storage stability and energy density when compared with liquefied or compressed hydrogen. When treated by reforming technology, it serves as a hydrogen source for fuel cells (Kolb 2008).

Methanol is converted to hydrogen-containing reformat by endothermic steam reforming (STR) (Kolb 2008) as shown in Eq. 1:

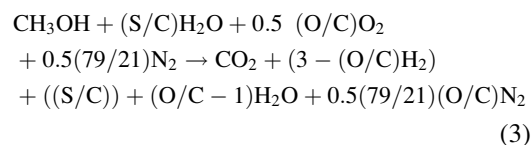


The highest hydrogen concentration in the reformer product is achieved at S/C 1. In order to reduce the carbon monoxide formation and to avoid coke deposition on the catalyst, a

surplus of steam is required. Therefore, practical systems operate at S/C ratios between 1.3 and 2.0. Because an excess of steam is required to maintain catalyst durability, apart from hydrogen and carbon dioxide, the reformat contains significant amounts of unconverted steam and to a lower extent some unconverted methanol and carbon monoxide. The latter is (at least for conventional Cu/ZnO catalysts) formed by the reverse water-gas shift reaction as shown in Eq. 2 (Fig. 1):



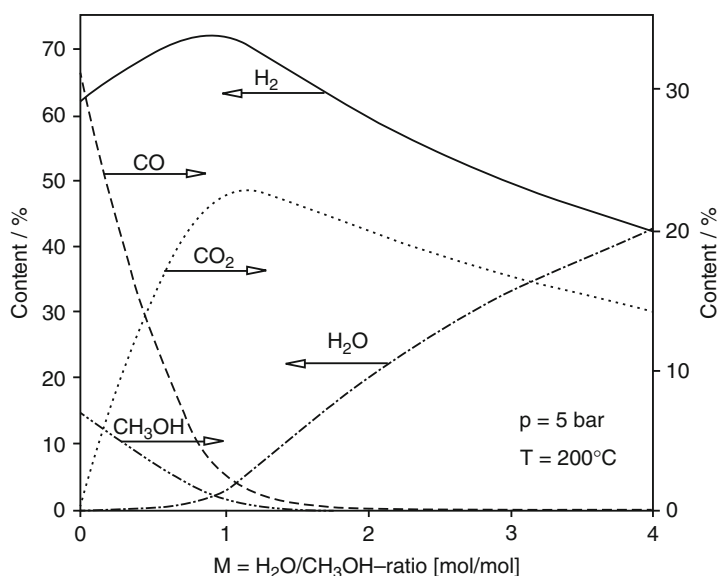
When not only steam but also air is fed to the reformer, the reaction is named oxidative methanol steam reforming:



S/C is the molar steam to carbon (here methanol) ratio; O/C is the ratio of atomic oxygen in the

Catalytic Methanol Steam Reforming,

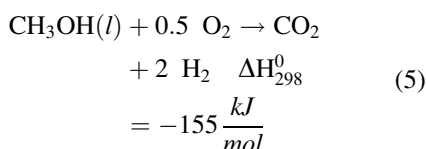
Fig. 1 Equilibrium gas composition of methanol steam reforming vs. S/C ratio of the feed; pressure 5 bar; temperature 200 °C (Schmidt et al. 1994)



oxidant to carbon in the fuel. The hydrogen content in the reformat is then derived from the following equation:

$$x(\text{H}_2) = (3 - (\text{O/C})) / (3 + (\text{S/C}) + 0.5(79/21)(\text{O/C})) \quad (4)$$

Oxidative steam reforming involves also the exothermic partial oxidation of methanol:

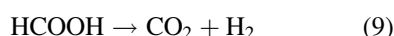
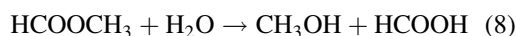


The enthalpy of the reaction at a temperature T is:

$$\begin{aligned} \Delta H_{298}^0 &= (1 - (\text{O/C}))\Delta H_R^T(\text{STR}) \\ &+ (\text{O/C})\Delta H_R^T(\text{POx}) \end{aligned} \quad (6)$$

For oxidative steam reforming with $\text{S/C} = 1.5$ and $\text{O/C} = 0.2$ at 350°C reaction temperature, the wet reformat has a hydrogen content of 57.4 Vol.%, and the reaction enthalpy amounts to 15 kJ/mol, i.e., the reaction is still endothermic. Heat losses are not included into the calculations above which means that additional energy is required to compensate for. In a practical, self-sustaining reactor, this energy could be gained from additional oxygen supply to the feed or by separate or integrated anode off-gas combustion.

Frequently observed by-products of methanol steam reforming are formic acid and methyl formate (HCOOCH_3), which are not tolerated by the anode electrocatalyst of low-temperature PEM fuel cells. They are intermediate products of methanol steam reforming (Takahashi et al. 1985):



Formic acid decomposition is a fast reaction (Jiang et al. 1993). Dimethyl ether is formed by

methanol dehydration and is also observed as a by-product:



The reaction is thermodynamically favored by lower reaction temperatures (Lwin et al. 2000).

Catalyst development for methanol steam reforming as hydrogen source for fuel cells had been mainly focused on ZnO-containing catalysts such as Cu/ZnO and Pd/ZnO (either supported by the ZnO itself or by alumina carrier) owing to their high activity and low selectivity toward carbon monoxide. However, these catalyst formulations show a number of drawbacks. Once converted into their active (reduced) state, Cu/ZnO catalysts show pyrophoricity when exposed to an oxidizing environment. At reaction temperatures exceeding 300°C , the catalyst deactivates, which originates from copper sintering. Cu/ZnO is an excellent water-gas shift catalyst, which is its current main industrial application field. Consequently, carbon monoxide is formed by the reverse water-gas shift reaction as soon as all the methanol is converted, which happens under conditions of partial load of a practical reformer reactor. Pd/ZnO catalysts are higher in activity when compared to Cu/ZnO, mainly because this catalyst type allows higher operating temperature. Even at reaction temperatures exceeding 300°C , the selectivity toward carbon monoxide remains low, because a Pd/Zn alloy is formed (Chin et al. 2002, 2003). However, Pd/ZnO catalysts are known to bear always the risk of metallic palladium formation, which results in carbon monoxide formation much higher than the values formed over Cu/ZnO or Pd/Zn alloy. Pd/ $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ and Pt/ $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts are an alternative to the catalysts discussed above (Men et al. 2010; Kolb et al. 2011). They are even more active than Pd/ZnO.

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Catalytic Reactions, Membrane Operations of

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Catalytic reactions (chemical, biochemical, photochemical, electrochemical, and photoelectrochemical) are promoted or enhanced in their rate by a catalyst. Most of the chemical catalytic reactions are heterogeneous; the catalyst is normally a solid, while reactants are in fluid phase. In the petrochemical industry, for example, the catalyst is usually composed of micro- or nanoclusters of a noble metal in a support, usually a metal oxide. In the fine chemical and organic synthesis, on the other hand, it is common that the reactions be homogeneous.

Membrane is a permselective medium or interface between two fluid phases. Membrane

processes can be synergistically combined with catalytic reactors targeting conversion, selectivity, or safety enhancements. These effects may be obtained by selective product extraction and purification, normally originating conversion and selectivity enhancements, or by segregated or distributed feed of reactants, aiming selectivity and/or safety enhancements. When a reactor is synergistically combined with a membrane process, the unit is called membrane reactor. Usually, membrane and reactor are integrated in the same housing (Marcano and Tsotsis 2002).

Membranes can be inorganic (metallic, ceramic, carbon) or polymeric in their nature. Membranes can be permselective or non-permselective. Permselective membranes are characterized by two important parameters: permselectivity, which describes the ability of the membrane to transport the different components of a mixture at different rates, and permeability, which quantifies the total amount permeated by the membrane when subjected to specific operation conditions, normalized by the membrane thickness. The mass transport mechanism is described by the sorption – diffusion models for dense and microporous membranes. For porous, different contributions should be considered: diffusive (activated, surface, Knudsen, and bulk) and viscous (Poiseuille flow). The contribution of each one depends on the operating conditions, pore size, penetrant mass and size and the surface, and penetrant nature (Basile and Gallucci 2011).

There are various potential industrial applications that take advantage of combining a catalytic reactor with a membrane process, integrated or not in the same device, operating either in liquid and/or gas phases. One of the main membrane studied functions has been the selective removal of components from the reaction medium. Biorefining and biofuel production, for example, take advantage of process integration of a bioreactor and a permselective membrane, as is the case of bioethanol and acetic acid production: the continuous removal of the main product from the reaction medium decreases or even eliminates the potential reaction inhibition (Ma et al. 2009;

He et al. 2012). Also the removal of fermentation inhibitors generated during the pretreatment process of lignocellulosic material for the second-generation bioethanol production is important, because of the negative impact in the ethanol yield and productivity and in the cell growth inhibition (He et al. 2012). Still in the selective removal of a reaction product from the reaction medium, it can be referred to as the selective removal of water in esterification reactions and the selective removal of hydrogen in dehydrogenation and water-gas shift reactions for a conversion shifting beyond the thermodynamic equilibrium based on feed conditions. In case of using palladium-silver membranes in the dehydrogenation and water-gas shift reactions, high-purity hydrogen can be obtained (Marcano and Tsotsis 2002; Basile and Nunes 2011).

The membrane can also play a role of a selective distributor, dosing a reactant along the reaction medium. This approach has been extensively used in consecutive-parallel reaction schemes, especially in partial oxy-dehydrogenation or oxidation of alkanes and oxidative coupling of methane, using dense ceramic or metallic membranes permselective to oxygen (silver, yttrium-stabilized zirconia, perovskites and related oxides, or composite membranes involving a mixture of ionic and electronic conducting materials, usually oxides and metals). Separating the hydrocarbon and oxygen feed, the reaction is carried on in much safer conditions, and the possibility of thermal optimization and oxygen concentration control along the reaction medium can be used to improve the selectivity for the intermediate desired oxygenated product. Though in less extension, also proton-conducting membranes have been considered as distributors for hydrogenation reactions (Marcano and Tsotsis 2002; Seidel-Morgenstern 2010).

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Further Reading

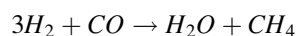
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Catalytic Reformer Off-Gas

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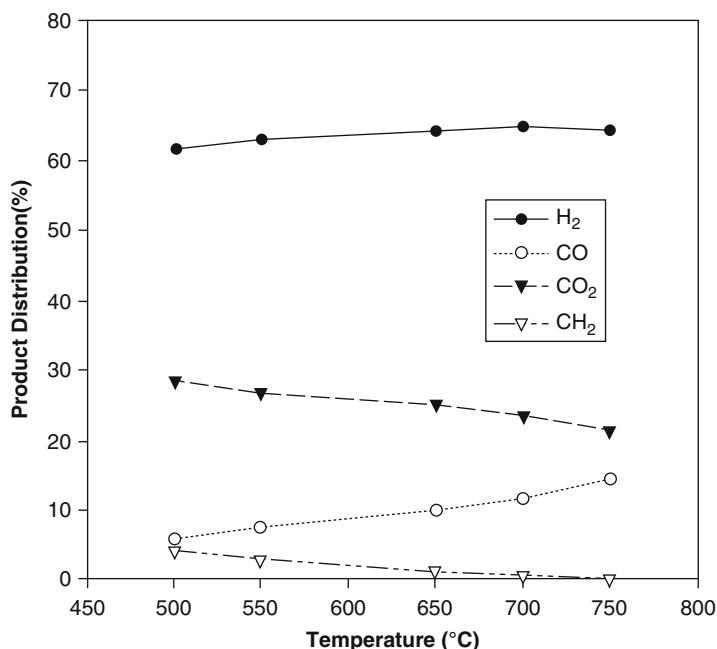
The product mixture formed during reforming of all kind of fuels such as hydrocarbons and alcohols is named reformat (Kolb 2008). The products of the reforming reaction are hydrogen and carbon monoxide (see entry “► Catalytic Reforming of Methane and Other Hydrocarbons”) unless methanol is applied as feed, which produces mainly carbon dioxide instead. The thermodynamic equilibrium of the reforming reaction itself is equivalent to full conversion of all kinds of fuels except for methane. The conversion of methane is limited by the equilibrium of the methanation reaction, which is the reverse reaction of methane steam reforming:



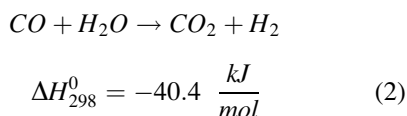
$$\Delta H_R = -253.7 \frac{kJ}{mol} \quad (1)$$

Catalytic Reformer

Off-Gas, Fig. 1 Dry reformat composition of isooctane partial oxidation in the presence of steam (nitrogen excluded); S/C = 3.0; O/C = 1.0; GHSV = 8,776 h⁻¹ (Moon et al. 2001)



The formation of methane is favored by lower temperature and elevated pressure, and therefore usually reformat from higher hydrocarbon reforming contains some methane (see Fig. 1). Methane is tolerated by most fuel cell types up to a concentration of 5 vol.%. Over sufficiently active catalyst and at reaction temperatures exceeding 600 °C, a second reaction occurs up to its thermodynamic equilibrium, the water-gas shift reaction:



The thermodynamic equilibrium of the reaction is favored by lower temperature (see Fig. 1).

Reformat contains besides hydrogen and carbon monoxide, depending on type of reforming applied, in case of steam reforming unconverted steam and for partial oxidation significant amounts of nitrogen originating from the air feed. Reformat originating from autothermal reformers contains both unconverted steam and nitrogen because both steam and air are fed to the process.

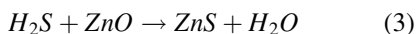
In case the reformat is dedicated as hydrogen supply for PEM fuel cells, the carbon monoxide content has to be minimized. The situation is different, when high temperature fuel cells such as SOFC are applied, because they are capable of converting carbon monoxide.

Further undesired by-products, which are frequently found in reformat originating from alcohol fuels, are acetaldehyde, ethers such as dimethyl ether and acetone. Light hydrocarbons, namely, ethylene and propylene, are frequent by-products of higher hydrocarbon reforming and an indicator for catalyst activity losses which then result in release of unconverted fuel later on.

Unconverted fuel and by-products are undesired components in reformat because they cannot be converted by fuel cells and reduce the efficiency of the energy conversion process. On top of that, they also poison the fuel cell catalyst in most cases.

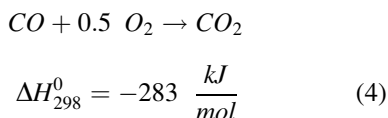
Because hydrocarbon fuels frequently contain sulfur components, which originate from intended odorant addition in the case of gaseous fuels such as natural gas (methane) and liquefied petroleum gas (LPG, propane/butane) and from the sulfur species present in the crude oil for higher

hydrocarbons, a sulfur removal is required when fuel cells are connected to the reformer. While gaseous fuels can be relatively easily purified through adsorption processes, sulfur removal from liquid fuels is more complicated, mostly owing to the lower adsorption capacity in the liquid phase. Because the reforming catalyst itself is normally rather sulfur tolerant and converts sulfur species to hydrogen sulfide, the sulfur removal can be performed through conversion over zinc oxide in the gas phase downstream the reformer:

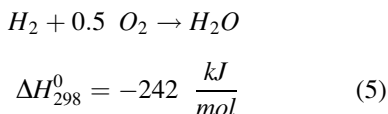


To convert the carbon monoxide which is poisoning for low-temperature PEM fuel cells to carbon dioxide, the water-gas shift reaction (see Eq. 2) is applied in dedicated reactors downstream the reformer, which operate at lower temperature to shift the equilibrium of the reaction.

To reach the low concentration of carbon monoxide required for low-temperature PEM fuel cells, which is in the range between 10 and 100 ppm, preferential oxidation (see Eq. 4) or selective methanation reactions (see Eq. 1) are applied:



The preferential oxidation reaction is accompanied by the undesired side reaction of part of the hydrogen present in the reaction mixture:



Usually preferential oxidation requires a minimum of excess air corresponding to an atomic oxygen to carbon monoxide O/CO ratio between 1.5 and 2.0. Under these conditions and full conversion of carbon monoxide, between 0.5 and 1.0 mol of hydrogen is lost for each mole carbon monoxide converted.

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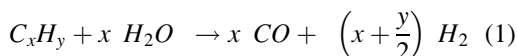
Catalytic Reforming of Methane and Other Hydrocarbons

G. Kolb

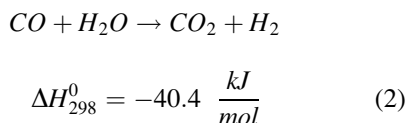
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Reforming of hydrocarbons is possible by conversion with either oxygen from air (partial oxidation), steam, or a combination of both named oxidative steam reforming. Only in the case of a self-sustaining operation of an oxidative steam reformer, when the partial oxidation reaction produces sufficient heat for preheating the feed, supply of the endothermic steam reforming with energy, and compensation of the heat losses of the reactor to the environment, this process should be named autothermal reforming (Kolb 2008).

The general formula of hydrocarbon steam reforming is provided below:

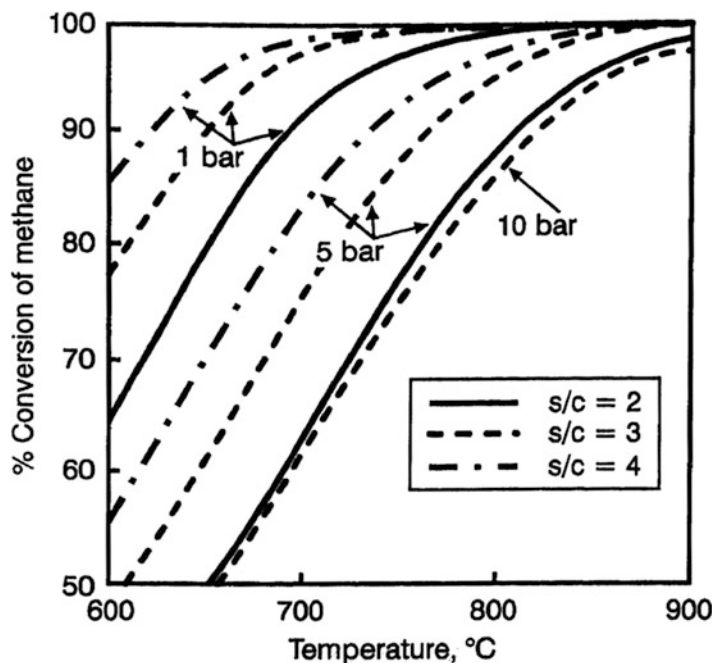


The product mixture of the endothermic reaction is named reformat, which contains besides hydrogen and carbon monoxide some unconverted steam, possibly unconverted fuel and carbon dioxide, which is formed through consecutive water-gas shift:



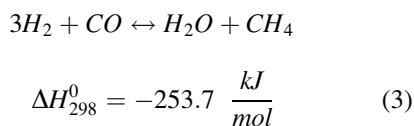
Catalytic Reforming of Methane and Other Hydrocarbons,

Fig. 1 Equilibrium conversion of methane steam reforming versus reaction temperature for different S/C ratios and system pressure (Joensen and Rostrup-Nielsen 2002)



This reaction obviously increases the hydrogen concentration of the reformat. Under operating conditions of hydrocarbon steam reforming over sufficiently active catalyst, thermodynamic equilibrium of water-gas shift is achieved.

Steam reforming of higher hydrocarbons shows also formation of methane through reverse methane steam reforming (methanation):

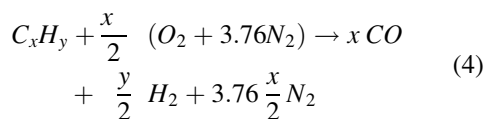


Increasing reaction temperatures and higher atomic steam to carbon (S/C) ratio increase the methane conversion according to the equilibrium of methane steam reforming reaction, while increasing system pressure has the opposite effect. The equilibrium conversion of methane steam reforming at various S/C ratio and system pressure is shown in Fig. 1. However, elevated pressure is required if the reforming process is combined with membrane separation and industrial steam reforming plants work at operating pressures exceeding 20 bar owing to similar

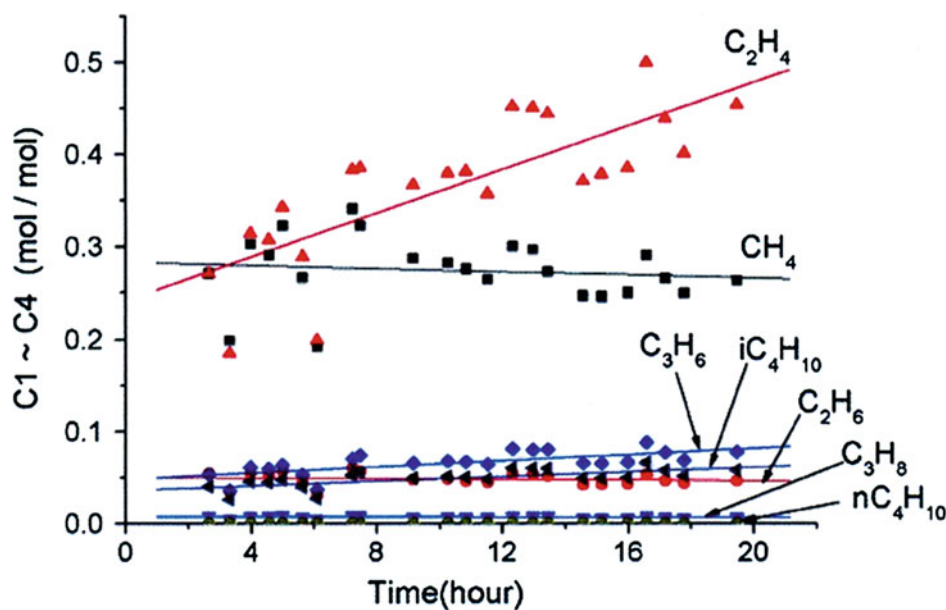
requirements of processes switched downstream the reformer.

While methane steam reforming is a reversible reaction, this is not the case for other hydrocarbon fuels.

Partial oxidation is the conversion of fuels to synthesis gas under oxygen deficient atmosphere:



The reaction is significantly faster than steam reforming. It requires only air feed and no water evaporation to raise steam, which simplifies the process. However, the carbon monoxide concentration is significantly higher compared to steam reforming, and the dilution through the nitrogen from the air is considerable. When hydrocarbons are converted by partial oxidation, some combustion occurs as an undesired side reaction (Joensen and Rostrup-Nielsen 2002), especially because an excess of air is fed into practical systems. The water produced by the combustion process allows water-gas shift to take place to a certain degree. Another typical by-product of partial oxidation



Catalytic Reforming of Methane and Other Hydrocarbons, Fig. 2 Ethylene formation versus time on stream for autothermal reforming of synthetic diesel (Kang et al. 2007)

is methane, which is formed according to reaction (3). Coke formation is a critical issue in partial oxidation. It is formed through the reaction of carbon monoxide with hydrogen, the Boudouard reaction, and cracking of higher hydrocarbons.

Figure 2 shows the breakthrough of unconverted fuel for oxidative steam reforming of synthetic diesel fuel. Catalyst deactivation during reforming of heavier hydrocarbons is indicated by the increasing formation of light hydrocarbons, predominantly ethylene. Yoon et al. (2009) explained the preferred ethylene formation in mixtures of paraffinic and aromatic feedstock by homogeneous decomposition of paraffinic components. The initial linear increase of the breakthrough is followed by an exponential increase later on.

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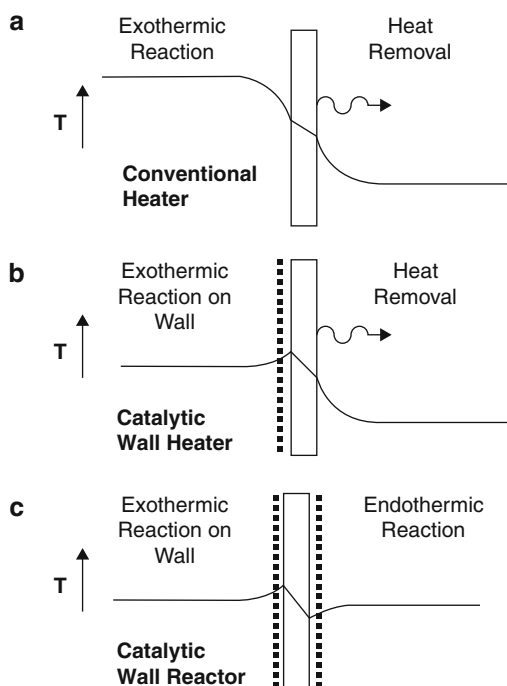
Catalytic Wall Reactor

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The micro-reactors discussed in the current section cover plate-heat-exchanger technology (see Fig. 1 (top)) with channels in the meso- and micro-scale, which are coated with catalyst in one or both flow paths, which makes them suitable for heterogeneously catalyzed reactions.

If only one flow path of the heat-exchanger is coated with catalyst, it transforms into a catalytic wall heater as shown in Fig. 1 (center). Catalytic



Catalytic Wall Reactor, Fig. 1 Threedifferent reactor concepts: conventional heater (*top*), catalytic wall heater (*center*), and catalytic wall reactor (*bottom*) (Redenius et al. 2001)

wall heaters improve the thermal management of exothermic reactions such as combustion and partial oxidation of fuels and of reactions related to CO removal from synthesis gas dedicated as hydrogen source for fuel cells, namely, water-gas shift and preferential oxidation of CO. Alternatively, endothermic reactions can be supplied with energy in such a reactor (catalytic wall cooler).

When the catalyst is coated onto the walls of the second flow path, the plate heat exchanger turns into a catalytic wall reactor as shown in Fig. 1 (bottom). This reactor type allows the direct coupling of exothermic reactions (such as steam reforming) and exothermic reactions (such as catalytic combustion). The heat source and the heat sink are then only separated by the few hundred to thousand micrometer metal foils between both catalyst coatings.

Micro-reactors for practical applications are chemical reactors carrying a multitude of channels with at least one dimension not exceeding one

millimeter. In such channels the flow regime is usually laminar, diffusion paths for heat and mass transfer are short, and the surface to volume ratio is small. Consequently surface effects dominate volumetric effects. Compared to macroscopic devices, a higher share of wall material exists. Thus the heat transfer through the wall material contributes significantly to the overall heat transfer and requires consideration when designing such reactors.

In practical micro-reactors suited for gas phase reactions, the channel dimensions are ranging between 250 μm and 1,000 μm height and from 250 μm to several millimeters width. Such micro-reactors carry normally thousands of channels operated in parallel. The high number and relatively large dimensions of the channels create a pressure drop in the order of few to few tens of mbar. The high degree of parallelization makes the scale up of such micro-reactors relatively simple provided that the equipartition of the fluid flow through all channels is ensured.

Obviously straight (micro-)channels are the simplest possible design. Other geometries such as sinusoidal channels or fin geometries have the potential for increasing the heat transfer. Increasing the heat transfer at constant pressure drop is not feasible for most channel geometries. Low pressure drop is critical for practical systems owing to the energy consumption required for the compression of gases.

A high heat conductivity of the heat-exchanger wall material reduces the efficiency of plate heat exchangers (Stief et al. 1999) especially if their length is similar to their width because isothermal temperature profiles will be created especially for construction material of high heat conductivity such as aluminum. It is therefore recommended to increase the heat-exchanger length and to reduce the wall material thickness and, if possible, to use construction material of low heat conductivity if a temperature profile is required in the catalytic wall reactor for reactions such as water-gas shift (Zalc and Löffler 2002; Baier and Kolb 2007).

However, heat-exchanger reactors for coupling exothermic and endothermic reactions such as catalytic combustion and steam reforming, respectively, should be operated under isothermal conditions. A cocurrent flow arrangement should

be chosen (Frauhammer et al. 1999) which has been proven for practical applications (Wichert et al. 2011; O'Connell et al. 2009).

The amount of catalyst which can be introduced into the plate-heat-exchanger reactor is a drawback more than counterbalanced by the better catalyst utilization through the improved heat and mass transfer. However, catalysts of higher activity are required to compensate the smaller quantities.

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- as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF), as these materials show the highest oxygen flux.
- The mechanism of oxygen transport through the MIEC membranes involves three different steps (Fig. 1):
1. The oxygen dissociation and reduction on the membrane surface (interface I)
 2. The incorporation into the crystal lattice as oxygen anions and the migration through the lattice via oxygen vacancy defect sites
 3. The combination of the oxygen anions on the membrane sweep side (interface II)

Thus the oxygen permeation flux through a MIEC membrane is determined by the bulk diffusion across the membrane and the surface exchange reactions.

The bulk diffusion resistance of the material can be improved by reducing the membrane thickness. The resistance from bulk diffusion plays an important role when the membrane separation layer is relatively thick. The oxygen flux is proportional to the reciprocal of the membrane thickness. So the flux can be improved by decreasing the separation layer thickness. The membrane surface exchange reaction becomes the rate-limiting step when the thickness of the separation layer is decreased beyond a certain value (L_C). Then the oxygen flux can still be further increased by improving the surface exchange kinetics. This can be done by applying a porous layer of the membrane material itself to increase the surface area or by adding a catalytic coating of a material with enhanced oxygen exchange properties to the membrane surface.

An example of the first case is shown in Fig. 2 where a 10 μm thick porous layer of BSCF is shown on top of the dense separation layer. The extra surface area improved the oxygen flux of the membrane by 210 %.

Pd has better oxygen exchange properties than LSCF itself. So another strategy, performed by Yacou et al., is coating the membranes with Pd

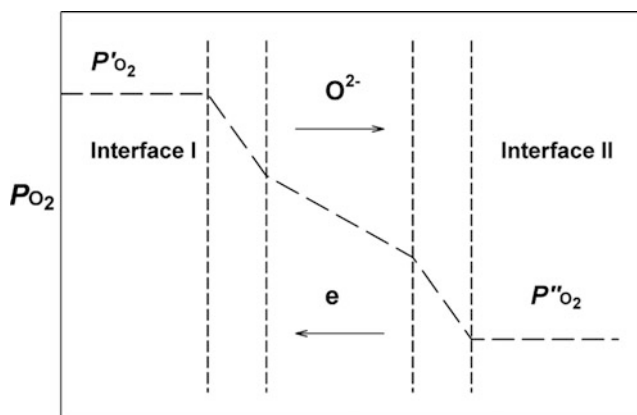
Catalytically Modified (Activated) MIEC Membranes

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Dense ceramic membranes which are made from mixed ionic and electronic conducting (MIEC) oxides can selectively separate oxygen from air at temperatures above 700 °C. The most used MIEC membrane materials are perovskites, such

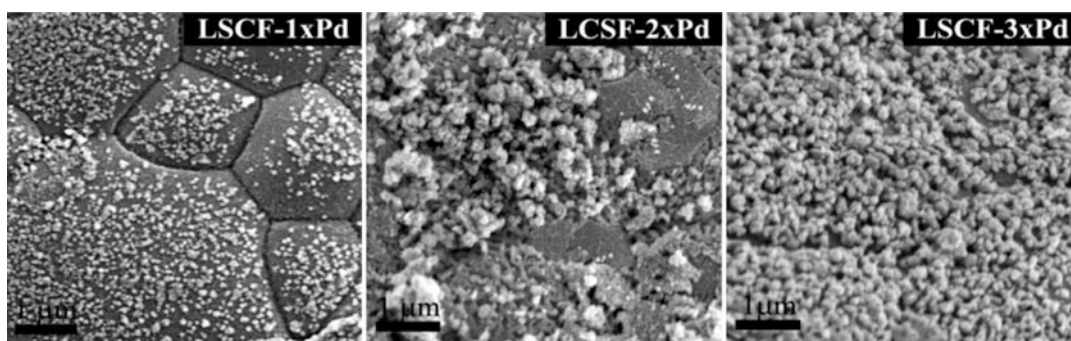
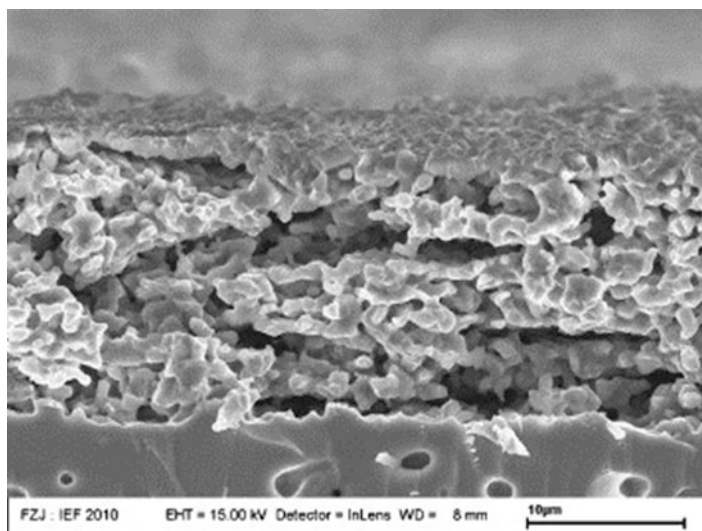
Catalytically Modified (Activated) MIEC Membranes,

Fig. 1 Different sections involved in oxygen transport during oxygen permeation (Sunarso et al. 2008)



Catalytically Modified (Activated) MIEC Membranes,

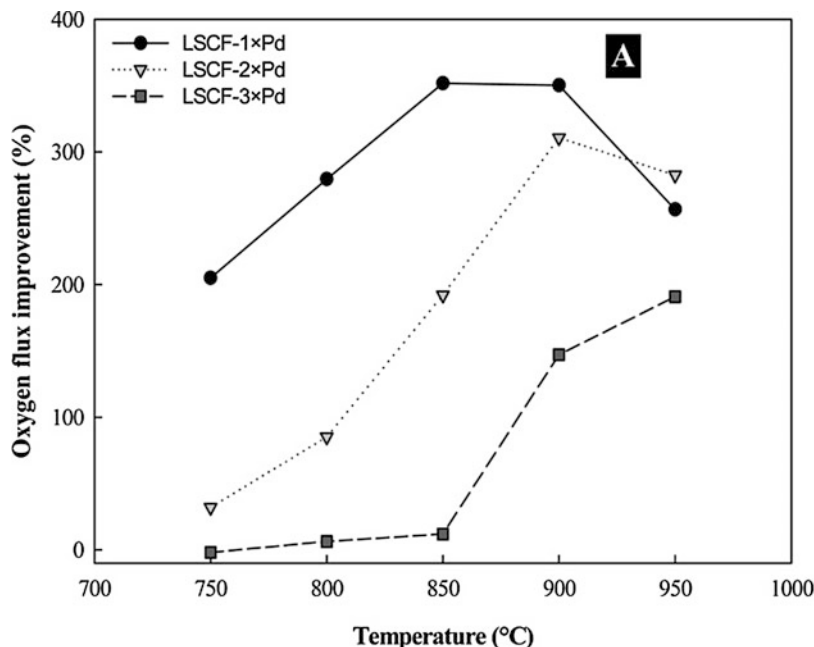
Fig. 2 Details of the morphology of the oxygen activation layer after the permeation test (Baumann et al. 2011)



Catalytically Modified (Activated) MIEC Membranes, Fig. 3 SEM micrographs of the surface of Pd modified LSCF membranes (Yacou et al. 2011)

Catalytically Modified (Activated) MIEC Membranes,

Fig. 4 Percentage improvement of the O₂ flux through some Pd modified LSCF membranes compared to the original LSCF membrane, as a function of the operating temperature (Yacou et al. 2011)



as shown in Fig. 3. This results in an even higher improvement ratio as shown in Fig. 4. This way the oxygen flux is improved by 350 %. So a small coating layer can have a big effect on the membrane oxygen flux without compromising the mechanical stability.

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Cell Adhesion

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Cell adhesion is the binding of a cell to a surface, extracellular matrix (ECM), or another cell using

cell adhesion molecules, which are integral membrane proteins that have cytoplasmic, transmembrane, and extracellular domains. The extracellular domains of adhesion molecules extend from the cell and bind to other cells or matrix by binding to other adhesion molecules of the same type (homophilic binding), binding to other adhesion molecules of a different type (heterophilic binding), or binding to an intermediary “linker” which itself binds to other adhesion molecules. Adhesion molecules belong to four major families: cadherins, immunoglobulin-like adhesion molecules, integrins, and selectins. Cadherins cause adhesion via homophilic binding to other cadherins in a calcium-dependent manner. As is the case for their role in desmosomes and adherens junctions, cadherins ultimately anchor cells through cytoplasmic actin and intermediate filaments. Immunoglobulin-like adhesion molecules are involved in both homophilic and heterophilic binding.

The well-studied members of this group are the neural cell adhesion molecules (N-CAMs), which are expressed predominantly in nervous tissue, and the intercellular cell adhesion molecules (ICAMs). Integrins are a diverse and large group of heterodimeric glycoproteins. The two subunits,

designated as alpha and beta, both participate in binding. Integrins participate in cell–cell adhesion and are of great importance in binding and interactions of cells with components of the extracellular matrix such as fibronectin. Importantly, integrins facilitate “communication” between the cytoskeleton and extracellular matrix, allow each to influence the orientation and structure of the other. Selectins are expressed primarily on leukocytes and endothelial cells and, like integrins, are important in many host defense mechanisms involving those cells. In contrast to other cell adhesion molecules, selectins bind to carbohydrate ligands on cells, and the resulting binding forces are relatively weak. Cell adhesion is believed to be the first and dominant step for cell growth.

Cells adhere strongly to some materials, but not to others (Hynes 2002). This is determined by the special structure of individual cell membranes and material surface properties. The initial cellular events that take place at the biomaterials interface mimic to a certain extent the natural adhesive interaction of cells with the extracellular matrix (Griffin and Naughton 2002).

Cell adhesion on a substrate such as a membrane is a multistep process that involves, in sequence, adsorption of ECM proteins onto the surface, recognition of ECM components by cell receptors, cytoskeletal rearrangements, and cell spreading. In particular, immediately after the biomaterial comes into contact with cell environment, protein adsorption to its surface occurs. This happens within seconds, long before the first cells reach the surface. Consequently, cells almost never come into direct contact with the material surface; they rather interact with the layer of adsorbed proteins. This layer mediates the cell adhesion and also provides signals to the cell through the cell adhesion receptors. The membrane properties (roughness, physicochemical, mechanical, and transport) especially the surface characteristics play an important role in the adhesion process (De Bartolo et al. 2004, 2008). Surface free energy, electric charge, and morphology might all affect cell attachment and its behavior either indirectly, e.g., by controlling adsorption of the proteins present in the culture

medium (or secreted by the cells), or directly, e.g., by guiding cell spreading with suitable surface topography (De Bartolo et al. 2002). Such properties resulted in being critical to cell–substratum interaction and have to be considered in the choice of material suitable for biomedical device.

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Cell Adhesion in Bioartificial Organs

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Binding of cells to a surface, extracellular matrix, or other cells in an artificial device is used to replace a nonfunctioning organ. Correct cellular adhesion is essential in maintaining multicellular structure and allows cells to interact dynamically with adjacent cells and the extracellular matrix. In bio artificial organs the cell adhesion process involves cell–cell and cell–natural or artificial matrix/material that plays essential roles in overall tissue architecture and proper physiological functions of the device.

The functional units of cell adhesion are typically multiprotein complexes made up of three general classes of proteins: the cell adhesion molecules/adhesion receptors, the extracellular matrix (ECM) proteins, and the cytoplasmic plaque/peripheral membrane proteins. The cell adhesion receptors are usually transmembrane glycoproteins that mediate binding interactions at the extracellular surface and determine the specificity of cell–cell and cell–ECM recognition. They include members of the integrin, cadherin, immunoglobulin, selectin, and proteoglycan (for example, syndecans) superfamilies. At the extracellular surface, the cell adhesion receptors recognize and interact with either other cell adhesion receptors on neighboring cells or with proteins of the ECM. ECM proteins are typically large glycoproteins, including the collagens, fibronectins, laminins, and proteoglycans that assemble into fibrils or other complex macromolecular arrays. Owing to their binding to adhesion receptors, they can also be tightly associated with the cell surface. At the intracellular surface of the plasma membrane, cell adhesion receptors associate with cytoplasmic plaque or peripheral membrane proteins. Cytoplasmic plaque proteins serve to link the adhesion systems to the cytoskeleton, to regulate the functions of the adhesion molecules, and to transmit signals initiated at the cell surface by the adhesion receptors. Several substrates different for the shape and physico-chemical properties are used for cell adhesion in artificial devices. Natural substrates such as ECM proteins (collagen, fibronectin, vitronectin, laminin) or polymers (chitosan, polylactic acid, polylysine, etc.) and synthetic substrates such as polystyrene, polycarbonate in the shape of scaffolds, gels, sponge, and membranes can be used in devices. Semipermeable membranes made from polyethersulfone, polysulfone, polycarbonate, polytetrafluoroethylene, modified polyetheretherketone, chitosan, polycaprolactone, polylactic acid, polyglycolic acid, and copolymers in flat and hollow fiber configurations are used for adhesion of different type of anchorage-dependent cells (hepatocytes, endothelial cells, neuronal cells, keratinocytes, progenitor cells, osteoblasts). In the case of bioartificial organs,

isolated cells are compartmentalized in a polymeric membrane which provides a number of important functions for the success of these devices. Membranes should act as barriers to immunocompetent species present in the patient's blood and should permit the rapid passage of key metabolites such as nutrients and oxygen from the surrounding to the cell compartment (Curcio et al. 2005). In such devices cells are contacting with membranes, the surface properties of membrane could affect the various bioresponses. Thus, one major approach of the materials scientists has been to try to influence the extent and the character of the cell response by modifying the surface composition and properties of the polymer. The response of cells to different material properties is a complex process and even minute changes in composition of the substrate produce amplified differences in cell responses. Although surface properties are often derived from the bulk properties of the materials, the bulk materials do not entirely define them, because the used substrates are coated with proteins almost immediately after implantation in the body or immersion in culture media. Surface chemistry and topography determine the identity, quantity, and conformational change of these adsorbed proteins. In particular, the roughness and pore size of polymeric membranes seem to play an important role since they have been shown to influence the viability and metabolic rates of cells (De Bartolo et al. 2008). Modification of surface chemistry including grafting of functional groups, peptides, and proteins represents a strategy to control cell responses in *in vitro* and *in vivo* systems. The most common peptide immobilized onto surfaces is RGD amino acid (arginine-glycine-aspartic acid) sequence that stimulates cell adhesion and growth since this peptide represents the minimal adhesion domains of the most ECM proteins (De Bartolo et al. 2005). The immobilization of specific moieties that interact with specific receptors of cell membrane is a challenge to enhance the selectivity of the membrane with respect to a cell type in order to employ it in tissue engineering for the reconstruction of a specific tissue. For example the immobilization of galactose motifs on the surface could enhance the specific interaction

with hepatocytes owing to the specific binding between the galactose moiety and the asialoglycoprotein receptor present on hepatocyte cytoplasmatic membrane (De Bartolo et al. 2006).

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- S. Ringer demonstrated that a beating animal heart can be maintained in salt solutions. First attempts of cell cultures are dated 1885, when W. Roux observed for a week embryonic chick cells using only a saline solution as medium. Therefore, it is in 1907 that the father of the cell culture technique R. Granville Harrison published experimental results on the growth of frog nerve fibers in a lymph clot held by the hanging drop method. Benefiting from the strict aseptic culture conditions introduced by A. Carrel, the nobel prize for medicine and physiology in 1992, this experimentation carried out for several weeks, led the way to the development of an enormous variety of cell culture techniques and to the progresses of the sterile conditions and the employ of culture media more and more completed and balanced in composition (Karp 2010). *Cell culture setup*. The specific requirements for a cell culture depend mainly on the final application the work is fated; therefore, there are some specific instruments and parameters that must be used and observed. To the basic equipment made of cell culture hood, incubator, water bath, centrifuge, refrigerator and freezer, cell counter, microscopes, liquid nitrogen, cryostorage container, and sterilizer, other additional supplies are requested, as vessels, reagents, media, pipettes, and so on. Moreover, either the working areas or the operators must ensure the aseptic conditions essential for avoiding biological and chemical contaminations. Contaminants like bacteria, yeasts, molds, viruses, and mycoplasma are not easy to eradicate and may waste the experimentations (Alberts et al. 2002).

Cell Culture

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“Cell culture” refers to a homogeneous group of cells able to grow and proliferate in controlled artificial environments for many generations. Generally derived from animal and plant, these eukaryotic cells are maintained in sterile vessels where a culture medium reproduces the nutritional and chemical-physical conditions of the native environment.

Some historiographical notes. The cell culture technique is only relatively a new science. Though the 1950s are considered the “cell culture years,” actually, already in the nineteenth century,

In a living organism, the cells survive due to the vascular system that brings the nutrients and removes waste product derived from the metabolism. In vitro, this function is entrusted to the culture medium. Classified in balanced salt solutions (PBS, Hanks' BSS, DPBS), basic media (MEM, DMEM), completed media (RPMI 1640, Iscove's DMEM, Leibovitz's L-15), and serum-free media (HAM F10, HAM F12), this specific isotonic solution is constituted by elementary substances and nutrients, as glucose, salts, amino acids, growth factors, carbohydrates, vitamins, lipids, and proteins, and a supplement of antibiotics is also requested for the inhibition of the

bacterial growth (penicillin 10,000 ug/ml; streptomycin 10,000 U/ml). A vitally important supplement of the medium is also the animal serum (FBS, NCS, HF). The serum, used in concentration of 5–20 %, is the main source of growth and adhesion factors (PDGF, EGF, IGF), hormones, lipids, and energetic sources. Moreover, it regulates cell membrane permeability and protects the cells from mechanical and chemical stresses, and its buffer power balances the pH value at 7–7.7. All the cell types need proper culture medium and supplements that must be refreshed regularly in aseptic condition to guarantee their survival (Alberts et al. 2002; Karp 2010).

Culture conditions. In artificial systems, the cell is traditionally cultured in plastic or glass vessels purposely made with different shapes and properties (flasks, Petri dishes, bottles). They are put in incubators where a temperature of 37 °C and a controlled atmosphere (95 % air – 5 % CO²) are set in order to mimic the native environment. In the field of tissue engineering and bioartificial organs, isolated cells are cultured on several types of biomaterials including polymeric and composite membranes, extracellular matrix components, and batch and dynamic systems. Depending on the cell types, there are two basic systems for growing cells in culture: the adherent culture system and the suspension system. The adherent culture system has been specifically developed for the growth of anchorage-dependent cells that derive from solid tissues and require to adhere to a substrate in order to survive and proliferate. On the basis of their morphology (shape and appearance) or on their functional characteristics, these cells are divided into two different typologies: the epithelial-like cells that appear flattened and polygonal in shape and the fibroblast-like cells, elongated and bipolar. The suspension culture, on the contrary, refers to the culture of anchorage-independent cells, as the blood or lymphatic cells that survive floating in suspension and assuming a spherical shape defined lymphoblast-like (Alberts et al. 2002; Karp 2010).

Isolation of cells. In order to set up a culture, the early stage is to acquire an already established cell line or strain or to isolate the desired cells

from a tissue fragment. When cells are immediately placed in a suitable culture environment after mechanical removal from a tissue, the so-called primary cultures are defined. To degrade the extracellular matrix responsible of the cell layer unity and to obtain a cell suspension, the tissue is enzymatically treated (collagenase, trypsin, protease), and the highly heterogeneous cell population is cultured in specific media able to separate single cell types interacting with the cytoplasmatic molecules expressed onto the plasmatic membranes (antigens). Despite having a finite life span due to the phenomenon of senescence, these cells proliferate until they occupy all the substrate available, reaching the confluence. At this stage, in order to avoid the degeneration and their death, the cells are enzymatically removed (e.g., trypsin, papain, collagenase in combination with EDTA) and transferred into a fresh growth medium in a new vessel (Hayflick 1998; Karp 2010). This procedure is called subculturing (passaging or splitting) and transforms primary cultures in “cell lines” or subclones, where the cells with the highest growth capacity predominate resulting in a degree of genotypic and phenotypic uniformity in the population. Moreover, when a subpopulation is further selected, this cell line becomes “cell strains” able to acquire additional genetic changes. The survival ability of normal cell cultures lasts only for a limited number of passages; however, some cells can become immortal due to a spontaneous or a viral-/chemical-induced modification. Acquiring the ability to proliferate indefinitely like the tumor cells, the characteristics of these transformed “continuous cell lines” are (i) the fast growth, (ii) the ability to grow up to higher cell density, (iii) reduced serum and anchorage dependence that allow the culture in suspension more than in adherent vessels, (iv) different in phenotypes from native tissue, and (v) stop expressing tissue-specific genes (Hayflick 1998; Alberts et al. 2002; Karp 2010). In order to preserve cell characteristic from further transformation or contaminations and to ensure the reproducibility of experimentation in time, a surplus of cells, derived from subculturing, can be treated with a cryoprotective agent (DMSO or glycerol) and stored at a temperature below 130 °C in liquid

nitrogen directly in the laboratories. Working stocks of cell lines are reposted in many cryopreservation banks including the American Type Culture Collection (ATCC) and the European Collection of Cell Cultures (ECACC) (Alberts et al. 2002).

The cell culture technology opens up new perspectives in many fields, as the manufacturing of vaccines and other products of biotechnology, and above all they became the turning point for the development of the tissue engineering, science entrusted of the study and production of artificial tissues and the regeneration of tissue and organs, either in 2D or 3D systems. Nowadays, the cell cultures are the “model system” and the perfect instrument for many applications: (i) production of pharmacological substances (antibodies, vaccines, growth factors, etc.), (ii) toxicity testing of drug effects, (iii) study of basic cell physiology, (iv) cancer research, (v) genetic engineering, (vi) tissue engineering and regenerative medicine, and (vii) gene therapy.

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Cell Encapsulation

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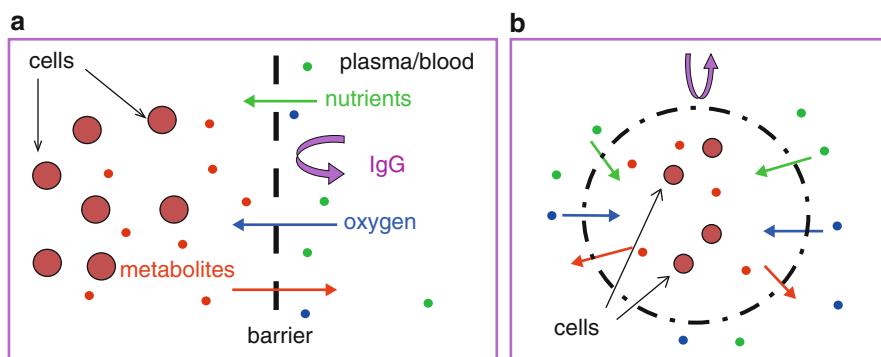
Encapsulation can be generally defined as a process that allows the entrapment of substances in a spherical-shaped porous material Chang (1964).

When sieving is ensured by an ultrathin membrane formed around a liquid core, the term of “capsule” is appropriate. When sieving is ensured by the whole core of the sphere, the term of “bead” is preferred and the porosity is homogenous across the structure.

In case of cell encapsulation for 3D tissue engineering, the goal is to host cells of a specific organ type into a porous scaffold in order to maintain their original functions and recreate a tridimensional organization mimicking the tissue to be replaced. Although many applications (such as pancreas, liver) have been developed in the last 30 years, there is still no clear consensus on the best choice for biomaterials and cells, whatever the organ type.

The materials hosting the cells should offer biocompatibility, adapted surface properties, and adequate porosity to allow the transfer of nutrients, oxygen, metabolites, and low molecular weight proteins such as albumin, but also immune protection and mechanical stability. They can be native or benefit from chemical and biological modifications to better mimic the cells’ niche and create micro-environments to control their response. Alginate is up to now the materials of reference. Alginate beads or capsules hosting cells are easy to produce by extrusion techniques, using coaxial air flow, electrostatic force, or vibrating nozzle to adjust the bead diameter. Encapsulation can be performed at room or body temperature, at physiological pH, and in isotonic solutions. The alginate bead or capsule might be coated in some approaches with a poly-L-lysine layer (PLL) to improve mechanical stability and reduce external porosity Orive et al. (2006). Other materials such as collagen, chitosan, gelatin, and agarose can also be employed, alone or in combination with alginate.

The spherical shape of beads or capsules provides them with interesting characteristics that can be considered advantageous to other porous scaffolds with plate or cylindrical (hollow fiber, for instance) geometries. This spherical shape is considered as the most efficient one for the promotion of mass transfer. Indeed, the sphere brings the best surface-to-volume ratio, leading to proper solutes’ bidirectional diffusion, provided that the sieving



Cell Encapsulation, Fig. 1 Principle of biohybrid constructs. (a) Description of the mass transfer expected between cell compartment and host. (b) Application to microencapsulation

properties of the material are tuned. The size of the beads or capsules related can be adjusted by the manufacturing process. Usually, their diameter does not exceed 500–1000 μm to avoid cell necrosis in the center. In addition, beads or capsules of this size can be easily frozen. Microencapsulation decreases cell damage during cryopreservation and allows thus an easy storage before use, leading to readily available encapsulated cells when needed.

The choice of cells depends on the targeted application as organ supply. For clinical application of tissue engineering, only primary cells (from animal or human origin) and cell lines have been employed. To reconstitute the functions of a failing organ or tissue, multiple pre-differentiated stem cell populations could be used and/or combined in biomaterials to form biohybrid constructs (Fig. 1).

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Cell Membrane

► Cellular Membranes

Cell Recycle Membrane Fermentor

Lidietta Giorno

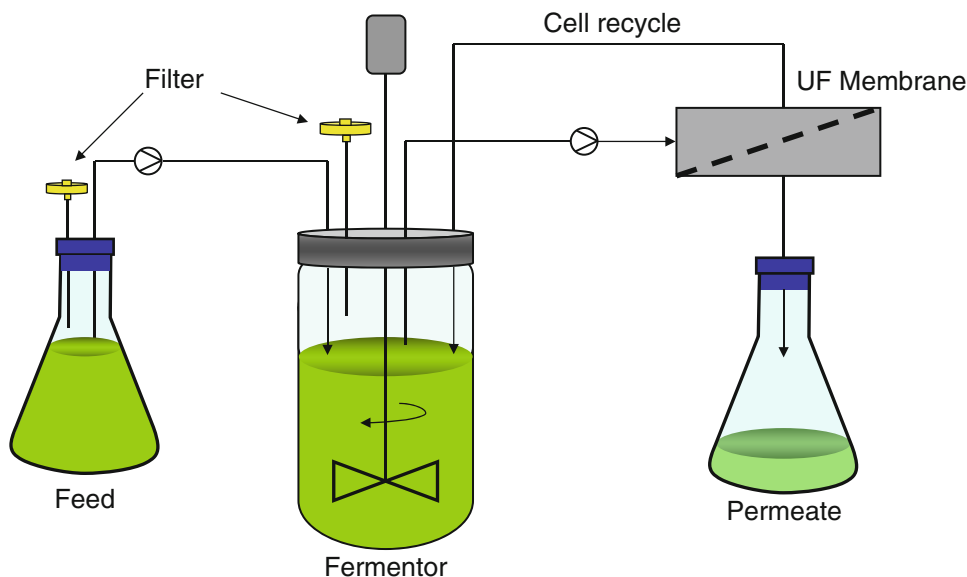
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Synonyms

“Cell-Recycle Membrane (Bio)Reactor” (CRMR); Continuous Membrane Fermentor (CMF)

A cell-recycle membrane fermentor is a hybrid setup of traditional fermentor combined with a membrane filtration process (Fig. 1). In literature they are also referred to as “Cell-Recycle Membrane (Bio)Reactor” (CRMR); continuous membrane fermentor (CMF); etc. All of them have the same basic concept of catalytic membrane reactors, which combine the chemical conversion (in the specific case a fermentation) with the separation of the product by membrane operations.

The system consists of a fermentor connected to a membrane separation unit. The system as a whole can be seen as a catalytic membrane reactor in which the biocatalyst is compartmentalized in the bulk reaction by the membrane module. Cells, macromolecules, and solids are retained by the membrane and recirculated to the fermentor. Product and other small molecules permeate through



Cell Recycle Membrane Fermentor, Fig. 1 Schematic of a cell-recycle membrane fermentor (or continuous membrane fermentor) (Drioli and Giorno, 1999)

the membrane and are removed from the fermentor. The volume of fermentor is kept constant by adding fresh feed at the same rate as the permeate flow rate. The product is diluted in the fermentor solution; concentration is reduced and product inhibition is avoided or at least limited. Since the substrate (glucose, sucrose) and low molecular weight nutrients permeate through the membrane together with the product, it is convenient to start the ultrafiltration process when the concentration of nutrients is decreased and that of product is increased. It must be taken into account that the concentration of substrate should not be lower than the limiting value for the survival of cells.

Since in a continuous fermentation mode, the microorganism is continuously fed to the reactor, its density is increased considerably. This fact allows the reactor to operate at high biocatalyst concentration. On the other hand, an optimal cell density must be maintained in the fermentor by using an appropriate bleed rate. In fact, high dense and viscous solutions are difficult to be treated by membrane processes. Furthermore, the fouling created by the macromolecules decreases membrane separation efficiency. This means that part of the fermentation broth has to be removed and

replaced with fresh medium at regular intervals of time to maintain good process performance.

The process variables in a continuous membrane fermentor are

- Flow rate of fermentation broth Q (l/h)
- Dilution rate, $D = Q_p/V$ (h^{-1}); where Q_p = permeate flow rate; V = fermentation volume
- Bleed rate, B (h^{-1})
- Starting time of ultrafiltration after onset of fermentation

These parameters have to be optimized case by case. In general, production rate is related to the dilution rate, in particular the production rate increases with increasing dilution rate. The productivity of continuous fermentation is higher compared to batch fermentation. However, final product concentration in the permeate is lower than the case of batch fermentation.

The economic advantage of high productivity process decreases rapidly when product concentration decreases. Lactic acid production by continuous membrane fermentor is interesting on an economic basis when production is on a relatively small scale and the lactic acid concentration is as

high as possible. The main reason for this is the high cost for water removal.

It is expected that the performance of the continuous membrane fermentor can be improved by integrating it in a continuous downstream process which selectively separates the lactic acid and recycles the substrate and nutrients, permeated through the UF membrane, back to the fermentor solution. For the downstream processing, electro-dialysis, membrane-based solvent extraction, and nanofiltration are among the most suitable methods.

When kinetic models for the growth and fermentation of a specific kind of cell or microbe on the corresponding substrate medium are available, mathematical modeling of membrane fermentors can be accomplished according to mass balances and the kinetics.

A steady-state mass balance on a continuous cell recycle fermentor over the vessel alone is as follows:

$$a' FX - (1 + a') FX + V\mu^* X = 0 \quad (1)$$

on cells, and

$$X' = Y D(S_f - S)/\mu^* \quad (2)$$

on limiting growth substrate to give a cell concentration value in the vessel equal to

$$X' = Y(S_f - S)/(1 + a' - Ca') \quad (3)$$

where

a' = recycle ratio

F = feed flow rate, $L^3 T^{-1}$

S_f = feed substrate concentration, ML^{-3}

S = substrate concentration, ML^{-3}

X' = cell concentration, ML^{-3}

X'_1 = cell concentration entering the membrane module, ML^{-3}

X'_2 = cell concentration in the recycle stream, ML^{-3}

μ^* = specific cell growth rate, T^{-1}

Y = organism yield coefficient, i.e., mass of cells formed/mass of nutrients

C = concentration factor

The specific growth rate (SGR) can be expressed as a linear function of the specific substrate utilization rate, KS , to give

$$SGR = Y.KS - D \quad (4)$$

where

KS = the specific substrate utilization rate, mass/mass time

D = the organism decay coefficient, $1/\text{time}$.

The kinetics of substrate removal in an anaerobic reactor actually determines the solid retention time (SRT) required for a given fermentation efficiency. In turn, the presence of the UF unit allows a fine control of SRT, making process control easier. When high biomass concentrations are achieved, longer SRTs can be maintained at lower reactor volumes.

The volumetric loading to a reactor, VL , is defined as

$$VL = Q Sf/V = Sf/t \quad (5)$$

where

V = reaction volume, L^3

Q = flow rate, $L^3 T^{-1}$

High biomass concentrations permit operation at higher volumetric loading rates. Reactor design can be carried out by estimating the value of volumetric loading necessary to achieve a given effluent quality. This design criterion is commonly used for biological systems where the evaluation of biomass concentration within the reactor is difficult. This is not the case with cell recycle fermentors, so the VL or the SRT approach can also be used as design criterion.

In continuous membrane fermentors productivity is a function of viable cell concentration within the fermentor. Cell recycle allows to operate at higher microbial cell concentrations than in conventional batch fermentors, reducing the volume required for a given productivity and hence the capital costs. On the other hand, the viscosity of the cell slurry increases with cell concentration, and concentration polarization phenomena are usually significant.

Systems such as rotating membrane modules, backflushing operations, etc. can be used to overcome fouling and expected concentration polarization problems. Provided cell resistance to shear stress, concentration polarization is usually controlled by operating the reaction system at high recirculation rates.

When concentration polarization occurs, permeate fluxes become invariant with the transmembrane pressure, and increases in the permeation rate can be achieved only by appropriate fluid dynamics conditions. The design of the UF membrane unit in the polarized regime must relate the flux to the optimal level of reactor volatile suspended solids (VSS) or total suspended solids (TSS) according to Michaels' gel theory, to give

$$J = K_S \ln (C_g/C_b) \quad (6)$$

where

K_S = the overall mass transfer coefficient, LT^{-1}

C_g = apparent solid concentration in the gel, ML^{-3}

C_b = concentration in the bulk, in the specific case, concentration of VSS or TSS, ML^{-3}

High recirculation and dilution rates help in maintaining low levels of inhibitory products.

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Cell Separation

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Cell separation is the process aimed at separating cells. Cells can be separated on the basis of different size, shape, physicochemical characteristics, specific molecules, or receptors present over their plasmatic membrane (Orfao and Ruiz-Arguelles 1996).

Traditionally cells are separated through centrifugation technique for the different density and size. This technique only requires the resuspension of the cells in an appropriate buffer and the knowledge of their approximate composition and density or size. Cells of different masses and densities are pelleted accordingly, with the densest cells pelleting first and at comparatively low centrifugation speeds, while the smallest, lightest cells require much faster speeds. The pellets can then be collected and resuspended in the desired buffer. Another method consists to use antibody which are able to recognize cell membrane proteins. All cells have an array of proteins on their surface membrane, some of which are found only on particular cells. The antibodies are often tagged with a fluorescent compound (fluorophore) so that the whole cell suspension can then undergo flow cytometry, which will identify and then isolate each cell individually. The antibodies can be also combined with a tiny magnet. The cells are then applied to a magnetic column that is capable of retaining these tagged cells when a magnetic field is generated within it. Cells can be separated through a biochemical method, which involves perturbing a biochemical process that is required by the cell for its growth and/or survival, and it should only be performed if a drastic manipulation will not detrimentally affect other steps in the experiment. Biochemical separations include blocking DNA synthesis, e.g., with hydroxyurea, and serum deprivation, i.e., growing cells in serum-free media for a specific amount of time. Membrane processes are used for separation of blood cells from other blood components through filtration. Cells are isolated by using membranes with suitable molecular weight cutoff that permit the passage of all components excluding only cells. Membrane filtration has also been used for the industrial separation of blood cells. Blood for transplantation is typically passed through membrane filters to eliminate leukocytes, which can help prevent infection by viruses such as human immunodeficiency virus and hepatitis C virus. Compared with other cell separation methods, membrane filtration is simple and inexpensive, and it is easy to maintain sterility during the process. Various porous polymeric membranes have been used for separation by filtration of different types of marrow

stromal cells (KUSA-A1 osteoblasts and H-1/A preadipocytes), due to the different cell size (Higuchi et al. 2005). Separation of hepatocytes and fibroblasts has been realized through surface-modified polyurethane membranes combining the filtration process with the use of negatively charged membranes (Higuchi and Tsukamoto 2004).

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Cell-Based Liver Support Systems

► Bioartificial Liver Support System (BLSS)

“Cell-Recycle Membrane (Bio)Reactor” (CRMR)

► Cell Recycle Membrane Fermentor

Cellophane

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Cellophane is made from regenerated cellulose in the form of thin and transparent films. The name of

Cellophane was derived from the French words cellulose and diaphane (transparent). Cellophane was invented by Swiss chemist Jacques E. Brandenberger while employed by *Blanchisserie et Teinturerie de Thaon* (Wikipedia free encyclopedia). In 1900, he started his first try. After almost 10 years, 1910, Brandenberger improves his film by adding glycerin to soften the material. By 1912 he had constructed a machine to manufacture the film and cellophane was patented that year (Carlisle 2004).

Cellophane manufacture process includes many steps. The first step is to dissolve cellulose in alkali and carbon disulfide to have a “viscose” solution. The second step is the extrusion of the viscose solution through a slit into a bath of dilute sulfuric acid and sodium sulfate to reconvert the viscose into cellulose film. The third step is the passing of the film through several more baths, one to remove sulfur, one to bleach the film, and one to add glycerin to prevent the film from becoming brittle.

The properties of cellulose membrane are intimately related to their structure and morphology which are mainly controlled by conditions, nature, and mechanism of coagulation. Therefore, to design desired morphology and properties, the cellulose membrane coagulated in different coagulation baths such as water and sulfuric acid aqueous solution (Fink et al. 2001; Hongo et al. 1999; Inamoto 1996; Manabe 1987; Abe and Mochizuki 2002; Bang 1999; Rosenau 2001). Owing to its high production costs and environmental pollution problems, it has great significance to develop simple producing process for cellulose membrane using new and powerful organic solvent *N*-methylmorpholine *N*-oxide (NMMO) to dissolve cellulose straightaway without any complex formation (Fink et al. 2001). The obtained cellulose membranes exhibited excellent mechanical properties and permeation characteristics (Fink et al. 2001; Abe and Mochizuki 2002; Bang 1999; Rosenau 2001).

Applications such as packaging for a variety of food items, base for such self-adhesive tapes, battery, and dialysis tubing (Visking tubing) and as a release agent in the manufacture of fiber glass and rubber products have been recognized.

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Cellophane Membranes

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Cellophane membranes are regenerated transparent cellulose membranes of high hydrophilicity, good mechanical properties, and biodegradability, biocompatibility, and gas barrier characters. The crystallinity and porosity of the membranes have been controlled through the regeneration conditions over the last decades. Recently, these characters are under control after investigating and using new

types of solvents for cellulosic materials especially ionic liquid solution. According to these characters, different applications of cellophane membranes have been recognized such as food packaging which represents the oldest one (Stocking and Mueller 1955). Hemodialysis cellophane membranes are one of the first applications in dialysis biological fluid (blood) to eliminate unwanted substances such as urea and creatinine. The cellophane membranes were used in planer form to dialyzed blood against electrolyte solution in artificial kidney (Mollison and Graydon 1977). Separation between two electrolytes as ionic barriers (battery separator) is one of the most known industrial applications of cellophane membranes. As a separator, it has “achieved the following objectives: (1) immobilization of the electrolyte by absorption in the cellulose, (2) elimination of the gases evolved in the operation of the cell, (3) prevention of mutual penetration of the active materials, and (4) homogeneous and reversible deposition of the negative active material (Zn) from the electrolyte (Claudia and Evans 1964)”. As ionic conductors, ion exchange cellophane membranes have been developed as fuel cell ion exchange membranes (Abu-Saied et al. 2012, 2013). The cellophane membranes act to conduct hydrogen ions and separate fuel from crossover to the anode compartment in the polyelectrolyte fuel cells. Due to cellophane membrane hydrophilicity, low nonspecific adsorption (Zou et al. 2001; Crawford et al. 1999), and good chemical stability, they were adapted as base for affinity separation chromatography membranes for proteins. Mohy Eldin et al. 2009 developed immobilized metal ion affinity membranes from poly(glycidyl methacrylate) grafted cellophane membranes for separation of β -galactosidase enzyme. Later on Mohy Eldin et al. 2011 developed immobilized metal ion affinity membranes from poly(methacrylic acid) grafted cellophane membranes for separation of His-Tag chitinase.

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Cellular Membranes

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Synonyms

Biological membrane; Biomembrane; Cell membrane; Plasma membrane

Cellular membrane (or biomembrane) is the biological membrane that surrounds and protects the cell and governs the transport of matter, energy, and information between the external and internal (and vice versa) of the cell.

Living cells are divided into several compartments and sub-compartments by a membrane. Each compartment has a specific function and structure and the interactions between compartments are highly regulated by specific signals. The corresponding delimited spaces or compartments are called organelles; in eukaryotic cells the main are endoplasmic reticulum, Golgi apparatus, nucleus, mitochondria, lysosomes, endosomes, and peroxisomes. Each membrane-enclosed organelle contains a specific set of proteins free or on the membrane surface that regulate many vital biochemical processes.

Cellular membrane is a complex system with multifunctional properties, acting as a separating/contacting barrier within or around cell and cell components. This system controls the selective transport of components and regulates the passage through the different compartments. In addition biological membranes have mechanical and elastic properties given by the interaction with intracellular skeleton and, if present, the extracellular cell wall (such as fungi, etc.).

In general, the biological membrane is formed by a continuous, water-impermeable, double layer of phospholipids containing a myriad of macromolecules and their complexes through which transport is promoted. According to the fluid mosaic model, the cell membrane is a two-dimensional fluid of proteins and lipids (Singer and Nicolson 1972).

The biological membrane is a dynamic and fluid structure, which implies that the molecules have a substantial degree of mobility in the two-dimensional membrane plane. This allows rapid lateral diffusion of lipids and proteins within the planar membrane surface. In contrast to lateral movement, the transbilayer or “flip-flop” diffusion of lipids from one leaflet in the bilayer to the other occurs very slowly. Transbilayer movement requires that a polar or charged head group leave its aqueous environment and move into the hydrophobic interior of the bilayer.

The fluidity of a membrane depends on its composition, the temperature, and how the different components are packed and organized in the membrane. In general, membrane fluidity is

decreased by lipids with long or saturated fatty acid chains, whereas lipids with short or unsaturated fatty acid chains tend to increase the fluidity of a membrane (Bittar and Bittar 1997). There are three major types of lipids found in the biological membrane: phospholipids, cholesterol, and glycolipids. Phospholipids form a bilayer in which the nonpolar regions of the lipid molecules in each layer face the core of the bilayer and their polar head groups face outward, interacting with the aqueous phase on either side.

Cholesterol is another important component found in the eukaryotic cell membranes. It has a rigid structure that stabilizes the membrane and reduces the natural mobility of the complex lipids in the plane of the membrane. Increasing amounts of cholesterol make it more difficult for lipids and proteins to move in the membrane.

Proteins are the second major component of the cell membrane, present in about equal proportion by weight with the lipids. Proteins are embedded in this bilayer sheet, held by hydrophobic interactions between the membrane lipids and hydrophobic domains in the proteins.

Membrane proteins can be classified according to their relationship with the lipid bilayer into two types: peripheral proteins (or extrinsic proteins) that are outside of the lipid bilayer without completely crossing the membrane and integral proteins (or intrinsic proteins) that cross the lipid bilayer only once or many times.

The proteins embedded in the cell membrane play a variety of roles. Many peripheral membrane proteins are enzymes, and many membrane-spanning integral proteins are carriers or channels (aquaporins) for the movement of water-soluble molecules and ions into and out of the cell. Another important role of membrane proteins is structural; for example, certain membrane proteins in the erythrocyte help maintain the biconcave shape of the cell. Finally, some membrane proteins serve as highly specific receptors on the outside of the cell membrane to extracellular molecules, such as hormones. The selective and regulated passage of molecules and ions across the cell membrane is an essential

component of cellular homeostasis. The selective passage of solutes across the cell membrane, a physiological property known as membrane permeability, is mediated by the presence of membrane transport proteins that span the phospholipid bilayer. Transport mechanisms may be distinguished thermodynamically according to their ability to mediate active or passive transport. The active transport is defined as movement of a solute across membranes from areas of low concentration to areas of high concentration. This process is done by carrier proteins and uses energy to transfer solutes against their concentration gradient. The most common source is the hydrolysis of ATP (adenosine triphosphate). Others include light energy and the energy stored in ion gradient. In addition, exocytosis and endocytosis are other transport mechanisms used for the movement of large molecules across the membrane. During exocytosis the macromolecules are contained within vesicles which fuse with the cell membrane to release their contents to the outside. In endocytosis the reverse takes place: the substances to be taken in by the cell are gradually enclosed by a region of cell membrane until a vesicle containing the substances is formed. Regarding the passive transport, it is defined as movement of a solute from a region of high concentration on one side of the cell membrane to a region of lower concentration on the opposite side (no energy is required to move a substance). The speed of solute diffusion depends on the difference of concentration, the size of the molecules, and the possible interactions of the diffusible substance with water. The diffusion across the membrane can be described by Fick's law:

$$J = -DA \frac{\Delta c}{\Delta x}$$

where J is the rate of diffusion, D is the diffusion coefficient, A is the membrane area, Δc is the concentration difference across the membrane, and Δx is the thickness of membrane.

The principal driving force for the passive diffusion of an uncharged solute across the plasma

membrane is the difference of concentration between the inside and the outside of the cell. In the case of an electrically charged solute, such as an ion, diffusion is also driven by the membrane potential, which is the electrical gradient across the membrane (Considine 2013). The cell employs three main mechanisms to carry out the passive transport:

- Simple diffusion is the passage of lipid-soluble solutes across the plasma membrane.
- Osmosis: in this process, the spontaneous movement of water across a membrane driven by a gradient of water concentration and the movement of water from a solution of high water concentration (low concentration of solute) toward a solution with a lower concentration of water (high solute concentration). Osmosis is a passive transport mechanism that tends to equalize the total solute concentrations.
- Facilitated diffusion is the movement of water-soluble solutes and ions through a channel or across the transmembrane transporter.

In addition to lipid and proteins, in the cell membrane, there are carbohydrates, which are attached to the proteins forming glycoproteins, or to some of the lipid classes, forming the glycosphingolipids. Protein-bound carbohydrate residues are on the extracellular surface of the cell membrane and take part in cell-cell interactions, including those of the immune system (Stein and Litman 2015).

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Cellulase in Membrane Bioreactors

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Membrane reactors have been developed mainly for catalytic reactions, using various membrane modules (e.g., flat sheet, hollow fibers). If biocatalysts (enzymes or cells) are applied, the equipments can be operated as membrane *bioreactors* (Drioli and Giorno 1999). One of the main advantages of the membrane bioreactors is that they make recovery and reuse of biocatalysts possible.

Usage of membrane bioreactors is especially beneficial for polymer degradation processes, where the small size product may have inhibitory effect, but can be separated easily by a proper porous membrane. This is the case of enzymatic hydrolysis of polysaccharides, like cellulose or starch. The long polysaccharide chain as well as the biocatalyst (enzyme or cell) are rejected by the membrane, while the product (glucose) passes through the membrane into the other phase. In such a system, continuous uptake of substrate and release of product without loss of biocatalysts can be achieved.

The huge amount of biomass produced annually worldwide is mainly composed of cellulose; its application for various purposes (industrial raw material, bioethanol, etc.) is extremely important nowadays. In these cases cellulose should be degraded by hydrolysis, resulting in glucose (monomer of cellulose). Enzymatic cellulose hydrolysis is carried out by various cellulases.

In general, hydrolysis of cellulose is more difficult to achieve than that of the other polysaccharides. The process is influenced by three main factors: the nature of the enzymes; the structure of the substrate; and the enzyme-substrate interactions (Mansfield et al. 1999). The action of the *cellulase enzyme system* includes three main

groups: endoglucanases, cellobiohydrolases, and cellobiases (β -glucosidase). These enzymes work in a synergistic mode to degrade cellulose, therefore it would be more effective to apply the whole complex enzyme system. One of the most effective cellulase systems can be obtained from the fungus *Trichoderma reesei*.

The main difficulty in cellulose hydrolysis is attributed to the *dual nature of the substrate*. The accessibility of the crystalline and amorphous regions is different; moreover, the solubility of the substrate is limited.

Finally in the *enzyme-substrate interactions*, it should be considered that hydrolysis of cellulose is a surface phenomenon. Before the reaction itself, the enzyme has to be bound to the substrate, i.e., the process requires the adsorption of the biocatalyst onto the insoluble substrate prior to the hydrolysis.

In a recent work, a membrane bioreactor was used with a hairy membrane layer (Bélafi-Bakó et al. 2006) that offered a special surface area for simultaneous adsorption of the substrate and enzyme. In this way the cellulose-cellulase layer formed provided a further advantage: diffusion resistance between the substrate and enzyme was reduced. Since solid particles present might cause troubles (fouling), it required special conditions for the construction of the membrane reactor. To avoid blockage, tubular type membrane module was used in the experiments. The simultaneous, reversible immobilization of the biocatalyst and the substrate onto the membrane surface was found to improve the efficiency of the process.

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Cellulose Derivatives

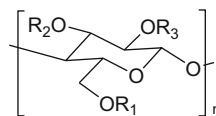
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Cellulose derivatives used in membrane fabrication are mainly referred to cellulose esters, in which cellulose acetate, cellulose diacetate, cellulose triacetate, and cellulose nitrite are typical components. There are other cellulose esters, including cellulose acetate propionate, butyrate, octanoate, benzoate, methyl carbonate, and methoxyacetate, which have also been used to fabricate membranes, with/without combination of cellulose acetate (Fig. 1). Membranes fabricated from single or multiple cellulose derivatives can be used in all fields of water purification, gas separation, and biomedical applications, where the morphology (e.g., pore size) and structure of the membrane can be flexibly adjusted through different preparation pathways (Ulbricht 2006).

Another widely used cellulose derivative is cellulose ether (e.g., ethyl cellulose), which has been demonstrated in fabrication of membranes for gas separations, such as hydrogen, oxygen, nitrogen, carbon dioxide, and methane (Mulder 1996).

Membranes fabricated from cellulose derivatives for separation applications offer several advantages: (1) a variety of cellulose derivatives with different physical and chemical properties are available; (2) good chemical resistance and mechanical properties are attainable; (3) cellulose derivatives are cost-effective; and (4) readily available surface functionalization pathway can offer new opportunities to generate new functional membranes. For example, the nanofibrous membrane fabrication approach (e.g., electrospinning to produce nanofibers) using cellulose derivatives, in combination with surface grafting of functional molecules and/or inclusion of nanoscale additives to create a nanocomposite structure, has expanded the family of cellulose membranes and opened many new separation applications (Ma et al. 2012).

Cellulose Derivatives,**Fig. 1** Cellulose derivatives for membrane fabrication (Turbak 1970)

$R_1 = R_2 = R_3 = H$	Cellulose
$R_1 = \text{CH}_3\text{CO}-$, $R_2 = R_3 = H$	Cellulose acetate
$R_1 = R_2 (R_3) = \text{CH}_3\text{CO}-$, $R_2 (R_3) = H$	Cellulose diacetate
$R_1 = R_2 = R_3 = \text{CH}_3\text{CO}-$	Cellulose triacetate
$R_1 = R_2 = R_3 = \text{NO}_2$	Cellulose nitrite
$R_1 (R_2, R_3) = \text{CH}_3\text{COCH}_2\text{CH}_2-$	Cellulose acetate propionate
$R_1 (R_2, R_3) = \text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2-$	Cellulose acetate butyrate
$R_1 (R_2, R_3) = \text{CH}_3\text{CO}-\text{C}_6\text{H}_5$	Cellulose acetate benzoate
$R_1 (R_2, R_3) = \text{CH}_3\text{COOCH}_3$	Cellulose acetate methyl carbonate
$R_1 (R_2, R_3) = \text{CH}_3\text{COOCH}_2\text{CH}_3$	Cellulose acetate methoxy acetate

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Central Nervous System in Relation to Membranes

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The central nervous system (CNS) is the most complex organ in the human body. It consists of two components, the brain and the spinal cord.

The spinal cord attends the communication pathway between the brain and the periphery, and like the brain, it is made of a gray matter, constituted by the bodies of the neurons, and a white matter, constituted by their myelinated axons, serving the impulse transmission. Moreover, a special blood-spinal cord barrier made of endothelial cells and astrocytes protects the spinal cord from the biological and chemical changes coming from the periphery. It was long believed that regenerative processes in the CNS were completely absent, then after an injury, the recovering of the axonal function was impossible (Kandel et al. 2000). In the early 1980s, therefore, it was discovered that CNS retinal neurons were able to regenerate in bioengineered devices of peripheral nerves, highlighting that the nearly absent ability to regenerate the central neurons does not lie in the cells themselves but in their surrounding environment. After physical trauma, hypoxic events, and degenerative pathologies, a rapid severing of the axons occurs, and in the spinal cord, cell death is recorded in high extent due to the lost electrolytic homeostasis and the accumulation of free

radicals and toxic factors that stimulate apoptotic events. While the peripheral nervous system (PNS) consists of a particular glial cell population able to proliferate and produce specific factors (BDNF, CNTF, GDNF) involved in the axonal regeneration across the area of injury, the oligodendrocytes constituting the main part of the central glia are not able to provide similar support after damage. In the injury site of the central nervous system, they secrete numerous inhibitor factors for the axonal regeneration, including NOGO proteins, NI-35, chondroitin sulfate proteoglycans (NG2), and keratan sulfate proteoglycans. The produced signaling factors that play neuroprotective and regenerative roles appear, then, to be not enough to oppose this inhibition and the inflammatory events occurring after the damage. Furthermore, astrocytes, another component of the central glia, became proliferative. In order to protect the severed site from external molecules and the spreading of apoptotic events, they form a tight network called a glial scar, which obstruct the axonal regeneration, creating a wall that axons and neurogenerative factors cannot overtake (Horner and Gage 2002). Thus, manipulation of the chemical and biological environment around the injured site represents the key of the treatment of the CNS damages. Specifically, in order to promote the axonal regeneration of the central neurons, the neurogenerative and neuroprotective factor levels should increase (Recknor and Mallapragada 2006). Nowadays, it is well known how neural cells respond to their microenvironment, enhancing adhesion, proliferation, and migration along the regenerating site. Smooth surfaces, patterned supports, and structures with high mass transport properties are the main characteristics allowing the neural regeneration both in vivo and in vitro systems (Morelli et al. 2012). Since decades ago, the gold standard of the nervous system injury treatment is the transplantation of nerve grafts able to substitute the malfunctioning or lost areas of the system. Despite the implantation of nerve grafts allowed to reach important results in the recovery of movement and sensibility of the PNS, the central nervous system is hard to be treated, particularly when inner regions of the brain are severed, then

new approaches appeared to be necessary for the treatment of the CNS injury. Due to the development of biomaterials and new processing methods for the scaffold design, tissue engineering and chemotherapeutic strategies are the main approaches for the development of regenerative strategies able to guide axonal outgrowth. A wide range of natural and synthetic biomaterials is available to prepare neural scaffolds and releasing devices (Tysseling and Kessler 2011). Different classes of biodegradable polymers are available, including polycaprolactone, polyurethanes, polylactic derived, polyglycolic acid, chitosan, agarose, polysaccharides, collagen and various ECM proteins derived. Due to their controlled bioerosion, these materials allow the design of different bioengineered devices, with different shapes and configuration purposely made for bridging the nerve growth or the factors' release. Any biomaterial used to prepare neural scaffolds possess, in addition to biocompatibility, an appropriate range of permeability, porosity, and biomechanical properties serving to avoid the compression of the regenerating nerves or the sudden collapse of the device in the treated site. Actually, three different strategies are available for the treatment of the CNS injury: the entubulation models, the drug delivery systems, and the cell therapy. All of them are categorized as membrane system devices due to their mass transport properties they allow the diffusion, release, and removal of the different factors involved after an injury.

The entubulation strategy consists in the transplantation of tubular scaffolds purposely made to mimic the peripheral nerve tissue. Considering that the PNS is characterized by a regenerative ability due to proliferation of glial cells and the secretion of neuroprotective and neuroregenerative factors, many devices have been developed with the aim of entrapping the central axons in a protect environment, where inhibitor factors are not allowed to pass through and neuroregenerative signals are enhanced. These bioartificial tubular nerve grafts are meant to ensure a correct diffusion of nutrients and oxygen and purposely designed with specific thickness, mechanical strength, dimension, and

porosity degree. Tubular nerve grafts made of PLLA, PCL and PGA, and collagen and chitosan already extensively used for peripheral nerve regeneration are nowadays applied for the treatment of CNS injury models, alone or in conjunction with brain-derived neurotrophic factor (BDNF) to promote the axonal regeneration (Recknor and Mallapragada 2006; Morelli et al. 2012). Cell-adhesive proteins such as collagen, laminin, and fibronectin, which bind strongly the integrin receptors on the cell surfaces, assist the nerve regeneration. They are often used to coat the lumen of the bioartificial channels or to modify the biomaterial used for the device preparation in order to enhance the cell response and the regenerative process. The patterning of polymeric tubular membranes with short oligopeptides derived from ECM proteins is another way to increase the neurite outgrowth and the cytoskeleton organization in the regenerating neural tissue. Along similar lines, the incorporation of hydrogels into the nerve tubes have been evaluated with encouraging results for CNS applications. Collagen, hyaluronic acid, agarose, alginate, chitosan, methyl cellulose, xyloglucan, matrigel, fibrin, polysia-based hydrogels, peptide hydrogels, as well as synthetic hydrogels, such as polyacrylamide and polyethylene glycol hydrogels, revealed to be the best alternative to the classical polymeric nerve guidance grafts. Bioengineered tubular scaffolds have been combined also with cells providing a promising new approach for the CNS injury treatment. Since 1998, it is well known that remyelination of central axons can be promoted by using Schwann and olfactory glial cells entubulated in bioartificial scaffolds, and moreover, Schwann cells, when seeded in combination with neurotrophic factors or hormones, facilitated the axon regeneration. Therefore, the strategy is to entubulate neural stem cells (NSC), which possess the ability to differentiate into neurons, astrocytes, or oligodendrocytes in presence of specific growth factors and appropriate chemical environment. Despite the risk of uncontrolled proliferation and some problems in the maintenance of cell viability, the use of the neural stem cells in membrane systems is still the most promising approach. *Drug*

delivery strategy. When a nerve guide or other bioartificial implants are not appropriate due to the impossibility to reach the severed central nervous area, the delivery system of neurogenerative and neuroprotective factors represent the alternative strategy. A few molecules of natural and synthetic origin showed to promote the neural regeneration. Steroids, minocycline, interleukin 10, erythropoietin, and neurotrophins, like NGF, BDNF, and CNTF, are just some of the neuroprotective agents implied in the inhibition of the inflammatory response, microglial activation, and apoptotic event after a central injury (Kandel et al. 2000). Induction of the regeneration-associated genes expression (RAGs) or the Rho-Rock pathway inhibition is some of the neurogenerative properties of the neurotrophins. Moreover, they promote their remyelination, the sprouting and growth of new neurons with functional recovery. Whether the factors possess neuroprotective or neurogenerative ability, the delivery strategies are the same. Growth factors, proteins, and drugs are encapsulated into the devices made of polymer, hydrogels, or proteins and injected in the spinal cord through epidural and intrathecal routes for the spinal cord regeneration. Hydrogels, liposomes, fibrin, collagen-based, and other polymeric delivery devices obtained from natural and synthetic biomaterials have been implanted subcutaneously near the spinal cord's injured site, allowing the continuous release of the neuroprotective and neurogenerative agents and the partial recovery of the axonal functionality (Zhong and Bellamkonda 2008). *Cell therapy.* The drug/biological delivery strategies are easy with respect to the entubulation methods, but in truth, they have one disadvantage: the constant drug dose is achievable only with reinjection of new delivery devices. The cell therapy, instead, relies on a longer production of the therapeutic factors through the cell stimulation in the injured site or the transplantation of autologous, allogenic, or xenogenic cells. Generally, the cell therapy is used for the treatment of the neurodegenerative pathologies and of the chronic pain. In order to implant the cells in the interested site, specific polymeric carriers are available.

A few trial models suggested that this kind of approach could enhance the chances of the patient to recover partially the neuronal functionality, opposing the symptoms and the cognitional problems. Polymeric membranes ensure a consistent advantage for that kind of application, which consists in the chance to control cell viability and the diffusion of nutrients and at the same time, the protection of the cellular population from the immunological reaction of the body. Genetically engineered cells encapsulated into hollow fiber membranes are able to produce and release ciliary neurotrophic factor (CNTF) in patients affected by amyotrophic lateral sclerosis. Parkinson's disease is another degenerative pathology treatable with the cell transplantation. In this case, dopamine-producing cells, dispersed also in different hollow fiber membranes of alginate, showed an increase of the recovery and an analgesic effect in the patient (Cho and Borgens 2012; Morelli et al. 2012). Therefore, the low percentage of cells surviving after implantation and the host rejection and the inflammatory response represent the main disadvantages of the cell therapy strategies. For this reason, despite the encouraging results available, the complexity of the central nervous system made the regenerative strategies always promising and not conclusive at the same time, and further investigation must be done in order to ensure a safe and functional approach for the recovery after an injury.

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Ceramic Membrane for Pervaporation

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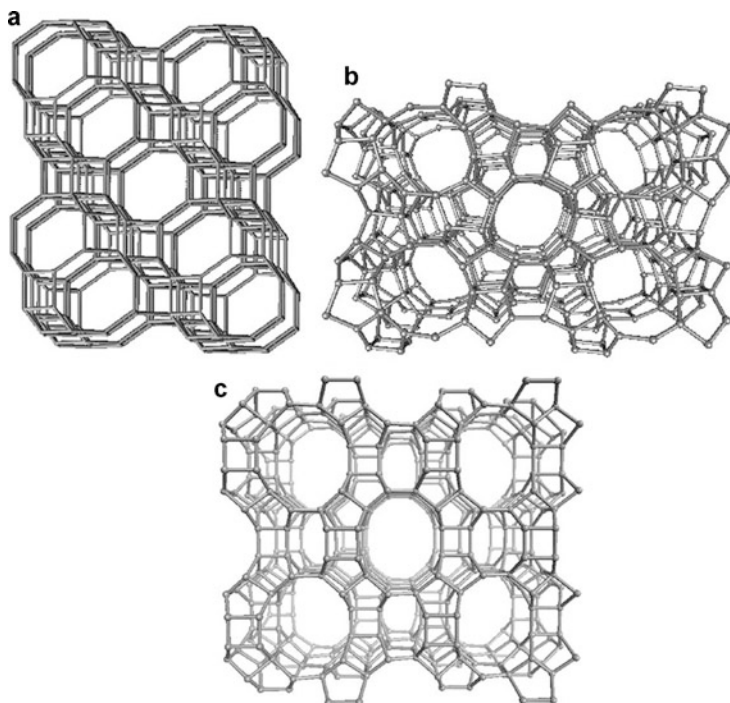
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Ceramic membrane for pervaporation, which is also called inorganic pervaporation membrane, belongs to inorganic microporous membranes made from silica, alumina, or zeolite, which has a narrow pore size distribution typically with pore diameter smaller than 1 nm. Inorganic pervaporation membranes have better structural stability without the problems of swelling or compaction relative to organic membranes. They usually can withstand harsh chemical environments and high temperatures (Wee et al. 2008). Most of the inorganic pervaporation membranes are asymmetrical, with several macroporous support layers providing the mechanical strength and a microporous selective top layer providing the selectivity. According to the membrane materials, inorganic pervaporation membranes generally have two kinds: zeolite membranes and silica membranes.

Zeolites are microporous aluminosilicate minerals with crystalline structures that have uniform and molecular-sized pores, which have been used extensively as catalysts and adsorbents. Zeolite membranes are synthesized by the deposition of continuous polycrystalline zeolite layers on porous supports, first reported by Suzuki in 1987 (Suzuki 1987). Zeolite structures are made up of TO_2 , where T represents tetrahedral framework atoms, such as Si, Al, B, Ge, Fe, and P. Most zeolites contain Si with other metals substituted

Ceramic Membrane for Pervaporation,

Fig. 1 Atomic stick representations for the frameworks of CHA (a), MFI (b), and MOR (c) zeolite structures. The nodes represent tetrahedral framework atoms and the sticks represent oxygen bridges (Reproduced from Bowen et al. 2004)



into the framework (Bowen et al. 2004). The zeolite pores are made from rings in the framework and are designated by the number of oxygen atoms making up the ring. Small-pore zeolites include those structures made up of eight-member oxygen rings, medium-pore zeolites have 10-member rings, and large-pore zeolites have 12-member rings. Examples of each of these are shown in the ball-and-stick representations of zeolite frameworks in Fig. 1 (Bowen et al. 2004). Several zeolite structures such as MFI, LTA, MOR, and FAU are widely reported as zeolite membranes used for pervaporation, due to their unique characteristic such as pore structure, adsorption properties, and their mechanical and chemical stability, as described in Table 1 (Baerlocher et al. 2002). Zeolite membranes are most often prepared by hydrothermal synthesis, including in situ synthesis, secondary growth method, continuous flow synthesis method, microwave synthesis, etc. (Wee et al. 2008). By utilizing the properties of molecular sieving and preferential adsorption, the current pervaporation applications of zeolite membranes mainly include alcohol (e.g., ethanol, isopropanol, butanol)

dehydration, organic/organic separations (e.g., xylene isomers, methanol/methyl-tert-butyl ether mixtures, methanol/benzene mixtures), and acid separations (e.g., acetic acid/water mixtures). In 2000, the first industrial-scale separation plant, based on NaA zeolite membrane for pervaporation dehydration of organic-water mixtures, was developed by Mitsui Engineering and Shipbuilding Co. Ltd. in Japan (Morigami et al. 2001). Until Now, NaA zeolite membranes have been commercialized by the Busan Nano-Research Institute Inc. (BNRI, a subsidiary of Mitsui), SMART Chemical company (UK), Inocermic GmbH (Germany), and Nanjing Jiusi Hi-Tech Co. (China) (Gascon et al. 2012). Unfortunately, NaA zeolite membranes are very sensitive to even the slightest acidity.

Another kind of ceramic membrane for pervaporation is silica membranes, which now are commercially available and developed by The Netherlands Energy Research Corporation (ECN) (Verkerk et al. 2001). The microporous silica membranes consist of four support layers of α - and γ -alumina, and the selective top layer at the outer wall of the tube is made of amorphous

Ceramic Membrane for Pervaporation, Table 1 Characteristics of the zeolite applied in membrane and an example of its application in pervaporation (Reproduced from Baerlocher et al. 2002)

	Zeolite			
	A	Y	ZSM-5	Mordenite
Structure type	LTA	FAU	MFI	MOR
Si/Al ratio	1	2.3	$8 \sim \infty$	4
Cations	Na	Na, Ca	Na	Na
Pore size	0.41 nm $\times$ 0.41 nm	0.74 nm $\times$ 0.74 nm	0.51 nm $\times$ 0.55 nm 0.53 nm $\times$ 0.56 nm	0.65 nm $\times$ 0.70 nm 0.34 nm $\times$ 0.48 nm 0.26 nm $\times$ 0.57 nm
Channel network	Three dimensional	Three dimensional	Three dimensional	One dimensional
Application	Dehydration of organic mixture	Separation of methanol/MTBE mixture	Separation of xylene isomers	Separation of benzene/ <i>p</i> -xylene mixture

silica. Silica membranes are mechanically and chemically robust. Not only are the silica membranes stable in a normal industrial environment, they can even be used to remove water from condensation reactions like esterifications, where strongly acidic conditions predominate. However, silica membranes are not stable against water, and thus the addition of oxides such as ZrO_2 and TiO_2 is often employed to improve the membrane stability toward water and alkali (Wee et al. 2008).

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Ceramic Membranes

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Ceramic membranes are made of ceramic materials, and to be specific, they must undergo a high-temperature sintering process to fall into the “ceramic membranes” category. Ceramic membranes belong to “inorganic membranes” category and need to be distinguished with other types such as metallic membranes or other hybrid inorganic membranes.

Membrane Types

Ceramic membranes can be divided to two types: porous and dense. Porous ceramic membranes have found their industrial usages in various filtration processes, while dense membranes are still at stages not more than pilot plants.

Porous ceramic membranes separate substances based on size exclusion; therefore, they can be further categorized as microfiltration, ultrafiltration, and nanofiltration membranes according to the pore size. Dense ceramic membranes separate one or two particular species (usually oxygen or hydrogen) based on the ionic conductivity of membrane materials, and they

often need to be used at high temperatures to increase their ionic conductivity.

Membrane Materials

Porous ceramic membranes are usually used in liquid filtration processes and mostly in aqueous environments; therefore, the membrane material must be compatible with water aside from proper mechanical strength. Most commonly used membrane materials are alumina, titanium oxide, zirconia, and silicon carbide. Alumina is predominant among all ceramic membrane materials because of its availability and relatively low cost, and it also provides strong mechanical properties, inert chemical nature, good thermal stability, and good surface hydrophilicity to the membranes. Zirconia or stabilized zirconia gives similar membrane characteristics as alumina membranes but much better mechanical properties; however, their price is also higher. Titanium oxide has better hydrophilicity and hydrothermal stability than alumina and zirconia, but its mechanical strength is moderate; therefore, titanium oxide is normally used only for the separation layer supported by alumina membrane supports. Silicon carbide membranes are more permeable than other ceramic materials and they often give impressive fluxes, but the major issue is the fabrication cost, which is much higher than others, due to the expensive raw material and extremely high sintering temperatures, as well as the protecting atmosphere required for sintering.

Dense ceramic membranes are used at high temperatures, and these membranes normally are made of ion-conductive materials or mixed ion and electron-conductive materials. For the former ones, an external circuit is needed to pass electrons to compensate the charge of ionic species when ions move from one side to the other side, and work can be done within the external circuit. This is the principle of solid oxide fuel cells (SOFCs), and the dense membrane acts as the electrolyte in a SOFC. For the later ones, electrons can pass the membrane directly, and separation of gas species can be completed by its own. The most important category of ion-conductive

materials is oxygen-ion conductor, for example, fluorite type oxides including fully stabilized zirconia and doped ceria, which are commonly used in SOFC, and perovskite type oxides that can be used alone to separate pure oxygen from air at high temperatures. Another important category is proton conductor, which also have attracted wide interests to use them in SOFC and high-temperature hydrogen separation.

Membrane Structure and Fabrication

Most ceramic membranes use asymmetric structures to obtain good strength and high permeation fluxes, especially for porous membranes, although symmetric structures are also found in dense ceramic membranes. In an asymmetric structure, a relatively thick and porous ceramic supporting layer is used, which is the source of mechanical strength of the membrane, and a thin separating layer is coated/deposited onto the support to provide selectivity for the membrane.

The supporting layer can be formed by extrusion, or by pressing, followed by partial sintering. The support is then coated/deposited with a desired separating layer. Different coating/deposition techniques have been developed for different purposes, such as dip coating and wash coating, sol-gel process, and chemical or physical vapor deposition techniques.

Applications

Porous ceramic membranes have been commonly used in water and wastewater treatment, food and beverage processing, pharmaceuticals, and chemical processing. The most widely used membrane types are microfiltration and ultrafiltration membranes, although the demand of nanofiltration ceramic membranes is also increasing in recent years.

Dense ceramic membranes have not really found their industrial usages, but some pilot plants of oxygen permeable ceramic membranes with a considerable scale are running in the USA and Europe, and some commercial SOFC products

are also available in the market. Some key technical obstacles need to be addressed before these dense ceramic membranes and the membrane-based technologies can enter into industrial usages, such as high-temperature sealing and system stability.

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Ceramic Multilayer Membranes

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A ceramic macroporous substrate is required to build multilayers over the substrates. Separation properties of a multilayer ceramic membrane normally depend upon the microstructure of the top layer (Li 2007). However, there may be necessity of intermediate layers between the macroporous substrate and top layer which give certain advantages like preventing sudden differences in pore size of support and top layer. The multilayering is carried out by a coating technique. When a tubular (or flat) substrate is withdrawn from a suspension or colloidal solution in a well-defined manner, a wet and more or less dense dispersion layer of well-defined thickness covering the substrate can be further processed through drying, calcining, or

sintering (Burggraaf and Cot 1996). In general, the process of multilayering involves preparation of multilayer through colloidal or polymeric sol-gel route. Precursors for colloidal sol-gel process may be organometallic compounds (e.g., aluminum or titanium based). This is hydrolyzed using excess of water. The sol is further peptized at certain temperature. It is also possible to prepare multicomponent sols. Supported gel layers are formed on membrane support by dip coating the supports with freshly prepared sols. Obtained gel layers are dried at room temperature followed by calcinations (Van Gestel et al. 2002).

Surface of the multilayer membrane can also be modified for different applications. Surface modification of hydrophilic γ -Al₂O₃/anatase-TiO₂ multilayer membranes by a silane coupling treatment in order to obtain NF membranes applicable in nonpolar solvents has been studied (Van Gestel et al. 2003).

Multilayer ceramic membranes have got huge potential for gas permeation applications which include separation of CO₂ or H₂ from methane and other hydrocarbons, adjustment of H₂/CO ratio in syngas, separation of air into nitrogen and oxygen, and recovery of helium and methane from biogas. Inorganic membranes also offer profound potential in applications for gas separation in a high-temperature catalytic reaction and are potentially useful for the separation of trace contaminants such as ammonia, hydrogen sulfide, and carbonyl sulfide from coal gasifier fuel gases (Othman et al. 2004).

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Ceramic Supported Polymer Composite Membranes in Pervaporation

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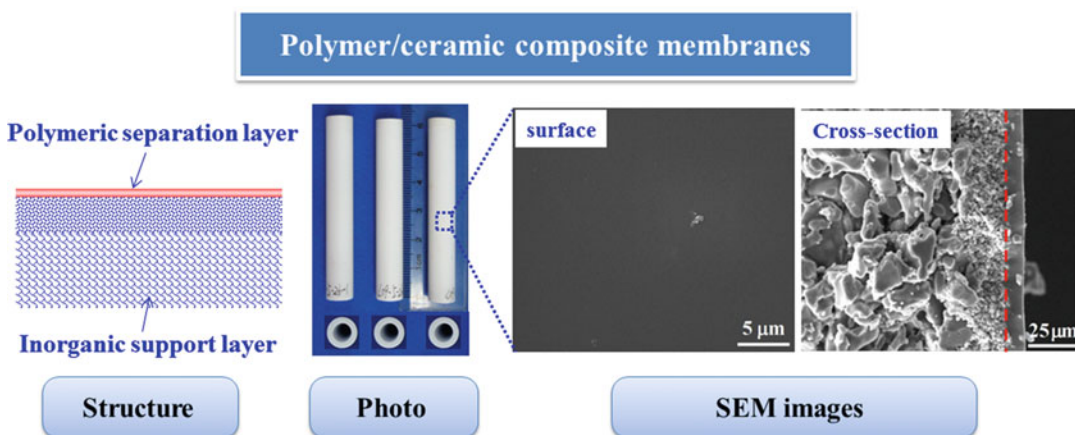
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Ceramic-supported polymer composite membranes in pervaporation are also called polymer/ceramic composite pervaporation membranes and are a type of composite membranes consisting of a thin dense polymeric separation layer and a porous inorganic ceramic support layer (as shown in Fig. 1). Theoretically, the polymeric materials used for preparing composite membranes are also suitable to produce polymer/ceramic composite membranes. For instance, polydimethylsiloxane (PDMS) (Xiangli

et al. 2007) and poly(vinyl alcohol) (PVA) (Zhu et al. 2010) are the typical hydrophobic and hydrophilic membrane materials, respectively. To keep a low transport resistance meanwhile ensures to obtain a defect-free selective layer; the mean pore size of the porous ceramic support ranges from a few nanometers to submicron size.

Like most composite membranes, polymer/ceramic composite membranes possess high selectivity from the polymeric layer and high flux from the porous ceramic support. Compared with traditional polymer composite membranes using organic support, ceramic-supported polymer composite membranes show advantages of chemical, mechanical, and thermal stability. Considering the practical application, the configurations of polymer/ceramic composite membrane usually include tubular and hollow fiber.

Polymer/ceramic composite membrane is always fabricated by dip-coating method in which a certain polymer solution is deposited on the outer or inner surface of the pretreated ceramic support. In general, some key preparing parameters such as polymer molecular weight, polymer concentration, cross-linking degree, dip-coating time, and surface properties of ceramic support play an important role in membrane preparation. The separation performance of polymer/ceramic composite membrane is determined by the integrity of the top polymeric layer and the thickness of the separation layer and interfacial layer created



Ceramic Supported Polymer Composite Membranes in Pervaporation, Fig. 1 Structure and morphology of polymer/ceramic composite pervaporation membrane

by the penetration of polymer solution into the porous ceramic support (Liu et al. 2012).

According to the membrane materials of the polymeric separation layer, the applications of ceramic-supported polymer composite membranes in pervaporation include organic compounds recovery from aqueous solution (Xiangli et al. 2008), biofuel production (Liu et al. 2012), gasoline desulfurization (Xu et al. 2010), solvent dehydration (Zhu et al. 2010), and hybrid process (Liu et al. 2011; Lv et al. 2012). For example, the PDMS/ceramic composite membrane can be applied for pervaporation recovery of ethanol from dilute water solution. With 5 wt.% ethanol/water in the feed at 40 °C, the membrane exhibits a high flux of 1.6–4.5 kg/m²h and separation factor of 6.5–8.5 with ethanol concentration in the permeate of 26–31 wt.%.

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CH₄/N₂ Separation

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The US pipeline specification requires an inert content lower than 4 % in natural gas. It is estimated that 14 % of US present proven gas reserves contain more than 4 % nitrogen (Baker and Lokhandwala 2008; Lokhandwala et al. 2010). The most trivial solution consists in diluting small flow rates of nitrogen-concentrated natural gas with main streams of natural gas containing a low concentration in inert gases. However, if this is not feasible (for instance, when all the surrounding gas fields contain high concentrations in nitrogen), it is necessary to install a nitrogen removal plant to comply with the regulatory natural gas composition specifications. Cryogenic distillation is the dedicated technology for large-scale nitrogen removal operations (60,000–600,000 Nm³/h capacity for operation life higher than 10 years). At the very end of the 1990s, 26 such plants were in operation on US ground (Lokhandwala et al. 2010). Two technologies have been recently introduced in order to solve this challenge at small and medium scale: pressure-swing adsorption (PSA) with molecular sieves (*Molecular Gates*® by the Engelhard company (Mitariten 2001, 2004) and gas permeation, which has been promoted by *MTR Inc.* since the end of the 1990s (Lokhandwala et al. 2010).

In the mid-1990s, *MTR Inc.* evaluated at lab scale (on 1–2 m² membrane modules) a wide array of composite membranes which selective membranes were made of various glassy or rubbery polymers (Lokhandwala et al. 2010). Intuitively, rubbery polymers proved to be more selective toward methane (due to its higher sorption, induced by its more condensable behavior than nitrogen), while glassy polymers, especially fluorinated ones, proved to be more selective toward nitrogen (due to diffusive selectivity).

MTR Inc. evaluated the economic feasibility of a membrane-based nitrogen removal operation on a 12,000 Nm³/h natural gas stream entering the process at 32 bar and containing 10 % nitrogen. The target of the membrane operation was to reach the 4 % nitrogen specification in the product gas while the waste gas was containing at least 50 % nitrogen and the overall methane recovery yield was to be higher than 93 %. Based on the performances of the various tested membrane materials, the study led to the conclusion that a single-stage membrane operation was not viable,

whether the membrane material was nitrogen-selective or methane-selective. Therefore, two-stage recycle schemes were studied involving only nitrogen-selective membranes or only methane-selective membranes or a combination of both. Only the use of methane-selective membranes proved to offer interesting performances (Lokhandwala et al. 2010), though the resulting process schemes were leading to significant extra cost due to the presence of two compressors: the first compression unit was used to pressurize the methane-enriched permeate produced by the first

Nitrogen removal (4 to 8% N ₂) (Nitrosep™, MTR Inc.)		1	2	3	4	5
Flow rate (10 ³ Nm ³ /h)		12	9.7	2.3	1.5	0,8
Pressure (bar)		70	14	?	?	5.6
Composition (% mol.)	N ₂	8	4	26	50	12.6
	CH ₄	92	96	92.5	50	87.4

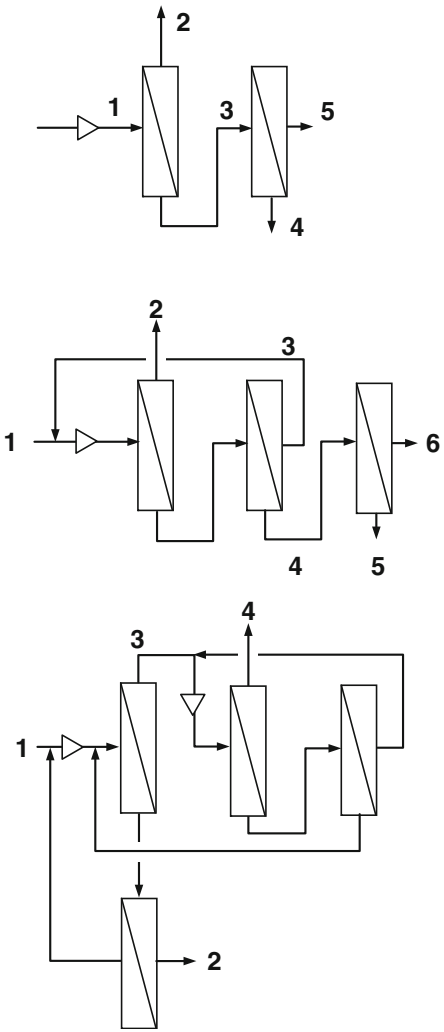
CH₄ recovery = 86 %
550 m² membrane area
690 kW (theoretical compression power)
stream 5 used as compressor fuel
stream 4 to flare

Nitrogen removal (8 to 15% N ₂) (Nitrosep™, MTR Inc.)		1	2	3	4	5	6
Flow rate (10 ³ Nm ³ /h)		12	9	?	?	1,9	1,1
Pressure (bar)		70	14	?	?	?	3.5
Composition (% mol.)	N ₂	15	4	8.7	50	65	26
	CH ₄	85	96	81.3	50	35	74

CH₄ recovery = 86 %
1,800 m² membrane area
1,860 kW (theoretical compression power)
stream 6 used as compressor fuel
stream 5 to flare

Nitrogen removal (15 to 30% N ₂) (Nitrosep™, MTR Inc.)		1	2	3	4
Flow rate (10 ³ Nm ³ /h)		12	9	?	?
Pressure (bar)		70	14	?	?
Composition (% mol.)	N ₂	15	80	11	4
	CH ₄	85	20	89	96

CH₄ recovery = 96 %
3,500 m² membrane area
2,680 kW (theoretical compression power)
part of stream 1 used as compressor fuel
stream 2 to flare



CH₄/N₂ Separation, Fig. 1 Permeation-based nitrogen removal from natural gas (After Lokhandwala et al. 2010)

membrane stage to the pipeline pressure, while the second one was aiming at boosting the pressure of the permeate stream issued from the second-stage in order to recycle it at the input of the first membrane stage. With this scenario, the total equipment investment cost was in a 4–8 million US dollar range (in 2009), while the required membrane area was approximately equal to 4,000 m². This appears to be acceptable by gas processors as the payback time of this type of installation was estimated to be 1 year.

The first field test of these membranes was therefore conducted with a 40 in-long module equipped with few m² of methane-selective membranes for more than 1 year on a shut-in gas well containing 15 % nitrogen operated by *Butcher Energy* in Southern Ohio. The performances of the spiral-wound module were very similar to those observed at lab scale, and its permeation properties remained unchanged for the first 6-month period. After this proof of principle, *MTR Inc.* designed different membrane-based nitrogen removal process schemes, trade-named *Nitrosep*[™], with various module/compressor configurations depending on the nitrogen concentration to be addressed (Fig. 1).

Up till now, 12 *Nitrosep*[™] units have been installed in the industry. Few examples depicting the applications addressed by this membranes process are listed hereafter:

- A very small unit was installed in Southern Kentucky in order to upgrade 200 Nm³/h of natural gas containing 7 % nitrogen. This two-membrane module unit was able to recover 80 % of the natural gas with a nitrogen content of 3.8 %. Part of the residue gas was used as compressor engine fuel, while the rest was vented.
- A much larger unit was installed in Rio Vista, California (14,000 Nm³/h treatment capacity). The membrane operation was aiming at upgrading a 16 % nitrogen containing natural gas to a gas stream offering 10 % more heating value (lowering thus the nitrogen content to 9 %). The membrane system involved three stages in series and allowed a methane recovery yield of 95 % for pipeline delivery.

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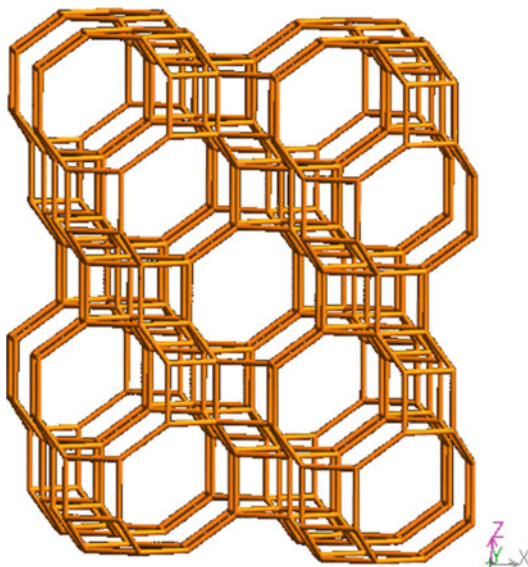
CHA Zeolite Membrane

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Zeolites are a class of crystalline aluminosilicates with highly regular and open microporous structures. More than 200 types of zeolite frameworks have been identified by the Structure Commission of the International Zeolite Association. Zeolite membranes combine the great advantages of inorganic membranes, such as temperature stability and resistance against solvents, with the molecular sieving effect.

Zeolite chabazite (CHA, where the three characters indicate the framework type) with Si/Al ratios of 2 ~ 3 is known to possess a three-dimensional pore system with large ellipsoidal cages (6.7 × 10 Å) that are accessible via eight-membered ring windows (3.8 × 3.8 Å). Figure 1 shows the framework structure of CHA zeolite (IZA web. 2013). High-silica CHA (Si/Al ratio > 5) has attracted great interest owing to its thermal and acid stabilities, and hence, application of this material to membrane has been widely investigated. The high-silica CHA zeolite membrane can separate light-gas mixtures of CO/N₂, CO₂/CH₄, H₂/CH₄, and H₂/n-C₄H₁₀ with notably higher selectivity than that allowed by the Knudsen mechanism (Kalipcilar et al. 2002). The high-



CHA Zeolite Membrane, Fig. 1 Framework structure of CHA zeolite (IZA web. 2013)

silica CHA zeolite membrane also exhibits excellent dehydration performance for water/alcohol mixtures (Hasegawa et al. 2010).

As the high-silica CHA zeolite has only been synthesized using expensive *N,N,N*-trimethyl-1-adamantammonium cation (TMAda⁺) as a structure-directing agent (SDA). Very recently, success was achieved in synthesizing high-silica CHA zeolites with Si/Al ratios of 5–21 from FAU zeolite using the benzyltrimethylammonium cation (BTMA⁺) instead of the expensive TMAda⁺. The high-silica CHA zeolite synthesized by the interzeolite conversion of FAU zeolite has superior acid stability (structural and compositional stabilities) as compared to the CHA zeolite synthesized using TMAda⁺ (Yamanaka et al. 2012).

Polycrystalline high-silica CHA zeolite membranes can be formed by the secondary growth of seed crystals on the outer surface of porous supports such as a porous α -alumina tube. Seed crystals are applied to the outer surface of the support tube by rubbing in order to implant the seed crystals for nucleation. The secondary growth solution with a chemical composition of $\text{SiO}_2:0.03\text{Al}_2\text{O}_3:0.2\text{BTMA}:0.1\text{NaCl}:10\text{H}_2\text{O}$ is prepared from the dealuminated FAU, BTMAOH, NaCl, and distilled water. Thereafter, a

hydrothermal reaction is carried out at 130 °C for 7 days using a Teflon[®]-lined autoclave. After cooling the autoclave, the support tube is recovered, washed with distilled water, and dried overnight in air at room temperature. Finally, the support tube is calcined at 550 °C for 20 h. Figure 2 shows scanning electron micrographs (SEM) of the surface and cross section of the CHA membrane on the α -alumina support (Yamanaka et al. 2012). The high-silica CHA-type zeolite membrane prepared on the α -alumina tube is connected with the stainless steel tube using heat shrink tubing, and the tube is subsequently set in the conventional batch-type pervaporation apparatus. An acetic acid aqueous solution (50/50 wt%) is used as the feed at 75 °C. The compositions of the feed and the permeate are determined by FID-gas chromatography (5MS capillary column). The permeation flux and separation factor, $\alpha(\text{H}_2\text{O}/\text{CH}_3\text{COOH})$, are calculated from the following equations:

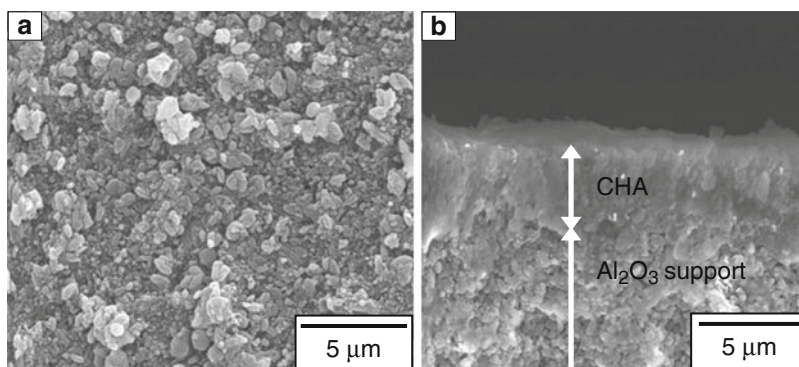
$$\text{Flux (kg/m}^2\text{ h)} = \frac{(\text{weight of permeate, kg})}{(\text{membrane area, m}^2) \times (\text{permeation time, h})} \quad (1)$$

$$\text{Separation factor } \alpha(\text{H}_2\text{O}/\text{CH}_3\text{COOH}) = \frac{[\text{C}_{\text{H}_2\text{O}}/\text{C}_{\text{CH}_3\text{COOH}}]_{\text{Permeate}}}{[\text{C}_{\text{H}_2\text{O}}/\text{C}_{\text{CH}_3\text{COOH}}]_{\text{Feed}}} \quad (2)$$

where the $\text{C}_{\text{CH}_3\text{COOH}}$ and $\text{C}_{\text{H}_2\text{O}}$ are the weight fractions of acetic acid and water, respectively.

The permeate flux and separation factor, $\alpha(\text{H}_2\text{O}/\text{CH}_3\text{COOH})$, are 7.9 kg/m² h and ca. 2500, respectively, and the membrane performance is identical to that of commercially available NaLTA zeolite membranes used for the dehydration of alcohol solution (Sato et al. 2008). The long-range time courses of both the separation factor and the flux are listed in Table 1 (Yamanaka et al. 2012). The CHA membrane prepared by the interzeolite conversion of FAU zeolites has high potential for use in the separation of water from acidic organic solvents and is not limited to acetic acid.

CHA Zeolite Membrane, Fig. 2 SEM images of (a) outer surface and (b) cross section of CHA zeolite membrane (Reproduced from Yamanaka et al. (2012) with the permission of Elsevier)



CHA Zeolite Membrane, Table 1 Time course of CHA-type zeolite membrane performance for dehydration of 50 wt% acetic acid aqueous solution at 75 °C (Reproduced from Yamanaka et al. (2012) with the permission of Elsevier)

Permeation time/h	$\alpha(\text{H}_2\text{O}/\text{CH}_3\text{COOH})$	Flux/kg/m ² h
1	2500	7.96
22	2480	7.88
77	2500	7.91
125	2380	7.80
170	2480	7.80

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Characterization of Porous and Dense Membranes

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Synonyms

Rejection

Membrane characterization is a key part in membrane research and development. In fact, the design of membrane processes and systems depends on reliable data relating to membrane properties. To identify a membrane type to be used for a particular process, it is crucial to know its properties.

Since membranes are very different in their properties and applications, a large number of different techniques are required for their

characterization. Some of the most important membrane characterization procedures described in the literature or recommended by membrane manufacturers are illustrated.

Porous micro- or ultrafiltration membranes are generally characterized in terms of their flux, their pore size, their pore size distribution, and their molecular mass cutoff. Other important characteristics are the nature of the membrane material (whether it is hydrophilic or hydrophobic or carrying positive or negative charges), the structure of the membrane (whether it is symmetric or asymmetric), and their mechanical, chemical, and thermal stability. The methods used to characterize porous membranes include simple filtration and retention measurements, microscopic techniques, surface tension measurements, and the determination of pore radii by liquid/gas or liquid/liquid replacement. The chemical and mechanical stability at various temperatures is usually measured in long-term tests. Which of the membrane characterization methods are applied depends on the use of the membrane.

The Pure Water Flux of Micro- and Ultrafiltration Membranes

A characteristic property of micro- and ultrafiltration membranes is their “pure water flux” or “pure water permeability.” The flux J through a porous medium is proportional to the applied hydrostatic pressure and inversely proportional to the solvent viscosity. It is expressed in Darcy’s law, which is given by:

$$J_v = \frac{L_p \Delta p}{\eta} \quad (1)$$

Here J_v is the membrane flux, L_p is the hydrodynamic solvent permeability, η is the viscosity of the solution passing through the pores of the membrane, and Δp is the applied pressure.

For the determination of the pure water flux, it is very important to use a certain water quality. Generally deionized or distilled water with a conductivity of $<5 \mu\text{S cm}^{-1}$, which is treated by

microfiltration to remove suspended materials, is used as a test solution. The flux is determined at different applied pressures and plotted as a function of the pressure. From the slope of the plot, the hydrodynamic permeability is obtained. Prior to the flux measurements, the membranes should be pressurized by filtration of pure water at a hydrostatic pressure that is at the upper limit of the recommended operating pressure for one to two hours to compress the membrane to a stable value that will not further deform when used at lower pressures. Possible preservatives, often present in membranes, must be eliminated by a washing procedure.

Some inorganic membranes, like Al_2O_3 -based types, show an apparent internal pore clogging when deionized water is used in the pure water flux measurements. In these cases an electrolyte solution is used for determining the membrane flux, e.g., a NaCl or KCl solution. Since there exists no standard method for the determination of the pure water flux, companies use their own standards, which makes a reliable comparison of pure water fluxes rather difficult.

Typical pure water fluxes of microfiltration membranes vary from 500 to 50,000 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, while pure water fluxes of ultrafiltration membranes vary from 50 to 800 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$.

In practical applications, fluxes are normally much lower, and a steep flux decline is observed during the first period of operation. This flux decline is mainly determined by membrane fouling which is generally more pronounced for microfiltration than for ultrafiltration.

Microscopic Techniques

A variety of microscopic techniques are used to study membrane structures, such as scanning electron microscopy, field emission electron microscopy, transmission electron microscopy, and atomic force microscopy. The advantage of these techniques is that direct visual information of the membrane morphology is obtained. The different microscopic techniques require different preparation methods and have different resolution. Scanning electron microscopy, e.g., has a resolution of

up to 5 nm and provides good information on the structures of micro- and ultrafiltration membranes including pore sizes and pore shapes. To reach a high resolution, high electron beam energy has to be applied, which can damage the membrane samples. Another problem is that in electron microscopy, a conductive layer must coat the samples. This is generally done in a high vacuum, which can lead to a change of the structure of membranes made from hydrophilic polymers.

The pore sizes and pore shapes of ultrafiltration membranes can also be determined by transmission electron microscopy which has a resolution of 0.4–0.5 nm or by field emission electron microscopy which has a resolution of 0.6–0.7 nm. The transmission electron microscopy technique requires a significantly more complex preparation procedure and is mainly applied to determine the surface porosity of ultrafiltration membranes (Fane et al. 1981). Because of the high resolution, pores in ultrafiltration membranes can be visualized by field emission electron microscopy (Kim et al. 1990).

Sample preparation for scanning electron microscopy and field emission electron microscopy analysis is relatively easy compared to the sample preparation for transmission electron microscopy. To visualize the cross sections of a membrane, e.g., it is immersed in ethanol or a water/ethanol mixture prior to cooling in liquid nitrogen. The sample is fractured providing a rather clean fracture and glued with conductive glue to a sample holder and sputtered with a thin layer of gold. The sputtered layer should be thinner than the structure features of the membrane to be studied. Recently, low-vacuum scanning electron microscopy, i.e., so-called environmental scanning electron microscopy, has become available which makes it possible to scan a sample without a conductive coating. However, the resolution of these microscopes is limited to magnifications of ca. 7500. Figures 1 and 2 show typical pictures of membrane structures that can be obtained by scanning electron microscopy techniques.

Besides electron microscopy, atomic force microscopy is also applied to study membrane surface structures. Atomic force microscopy has

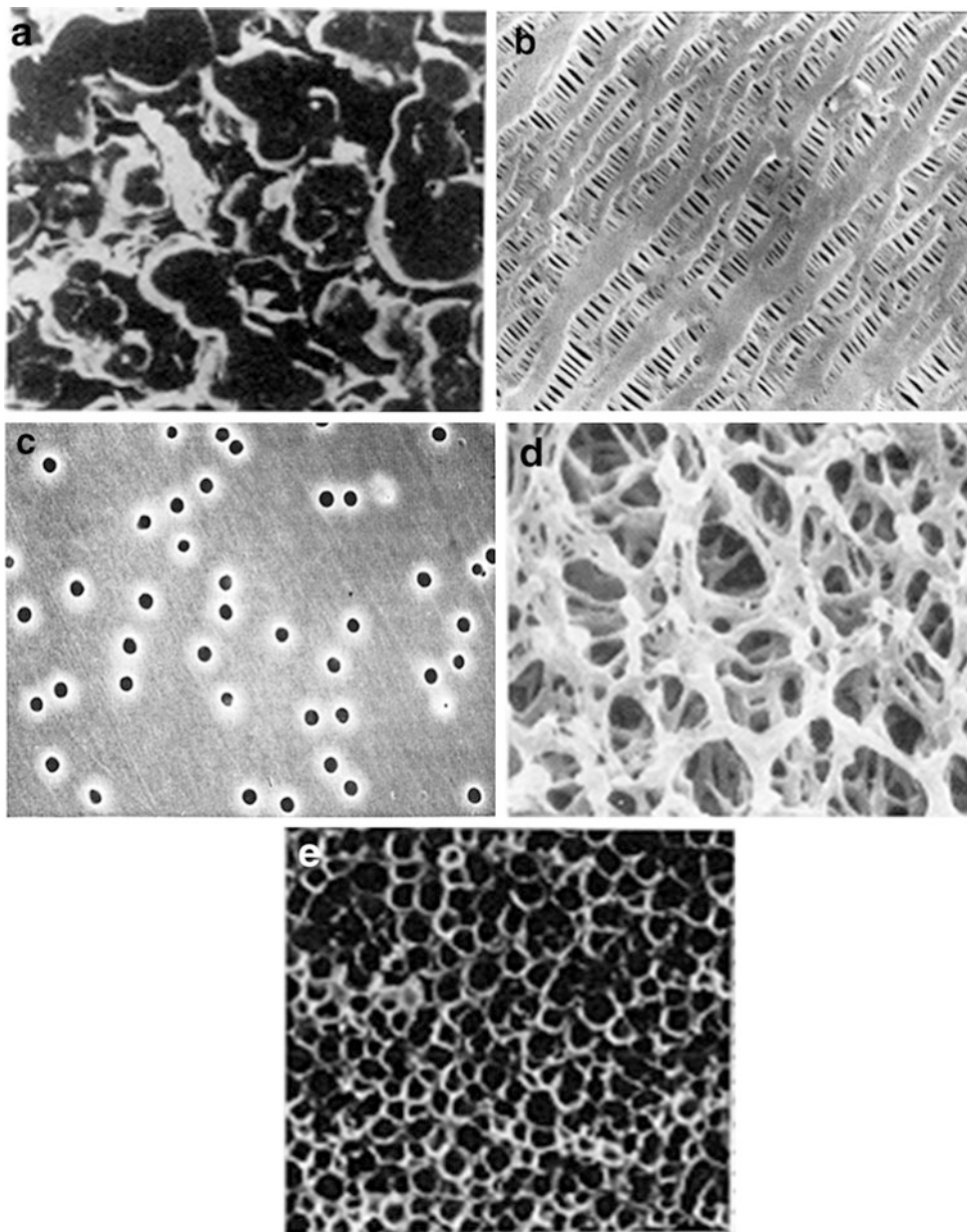
a resolution of ca. 1 nm (Fritzsche et al. 1992; Hilal and Johnson 2010). Sample preparation is fairly simple, since no conductive coating is required. Therefore, samples need not be dried and exposed to vacuum. AFM can operate in air and liquid phases; therefore, membranes can be studied in the environments used during their operation. This is very valuable for determining influence of physical-chemical parameters (such as pH, ionic strength, charge) and functional molecules on membrane surface properties.

The Mechanical Properties of Membranes

The mechanical stability and swelling behavior of the membranes is determined by the degree of cross-linking or crystallinity of the polymer matrix and the concentration of the fixed charges. The structure of membranes based on a highly crystalline polymer such as the fluorocarbon polymers are studied using transmission electron microscopy and small angle X-ray diffraction (Gierke et al. 1982). The degree of cross-linking is closely related to the swelling behavior and the mechanical properties of the membranes. But it also affects the permselectivity. Infrared spectroscopy measurements can provide some information on the type and degree of cross-linking of ion-exchange membranes.

A mechanical characterization of ion-exchange membranes involves the determination of its swelling and dimensional stability in different test solutions and tensile strength and hydraulic permeability measurements. All mechanical characterization tests should be carried out with well-equilibrated membranes in a controlled environment. The tensile strength and information concerning the plastic or elastic deformation of a membrane is obtained from a stress versus strain diagram as shown schematically in Fig. 2.

The strain versus stress curves of ion-exchange membranes generally show three distinct areas. At relatively low strain, the membranes show elastic deformation; with increasing strain, the membranes show plastic deformation, and at a certain point they break. Since the mechanical properties



C

Characterization of Porous and Dense Membranes, Fig. 1 Scanning electron micrographs of (a) a sintered membrane prepared from a polymer powder, (b) a membrane prepared by stretching an extruded polytetrafluoroethylene film perpendicular to the direction of extrusion, (c) of a capillary pore polycarbonate membrane made by

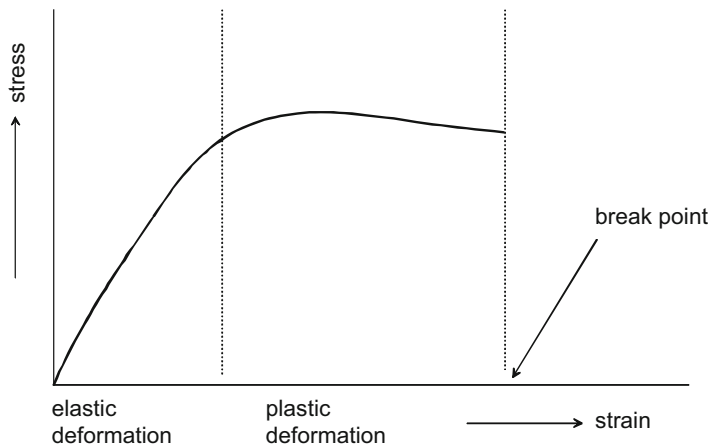
track etching, (d) a porous cellulose nitrate membrane prepared from a homogeneous polymer solution by water vapor precipitation, and (e) a porous polypropylene membrane precipitated by thermal gelation from a hot polymer solution

of membranes generally change drastically with the water content of the membranes, they must be determined with dry membranes and with

membranes equilibrated in water or different solutions similar to those used in practical applications.

Characterization of Porous and Dense Membranes,

Fig. 2 Stress versus strain diagram of a membrane sample indicating the elastic and plastic deformation and the breakpoint



The swelling of membranes depends on a number of different parameters such as the nature of the basic membrane polymer, the nature of the ion-exchange groups and their concentration in the membrane, the counterions, the cross-linking density, the homogeneity of the membrane, and the composition of the solution with which the membrane is in contact. Especially the concentration of the solution has a significant effect on the water sorption of the membrane because of osmotic effects that are directly related to the chemical potential difference of the water in the membrane and in the solution. The state of the water in the membrane can also be rather different. Part of the water is so-called “free” water. Another part of the water is strongly bound within the hydration shell of the counterions and the fixed charges of the membrane, while again another part is more loosely bound to the basic polymer matrix. The different water structures in ion-exchange membranes are studied by differential scanning calorimetry, infrared spectroscopy, and nuclear magnetic resonance (Komorowski and Mauritz 1982). Studies of the water structure within the membrane and its interaction with the membrane polymer, fixed charges, and counterions require more sophisticated spectroscopic measurements. The total water uptake of the membrane in equilibrium with an electrolyte solution, however, can be determined quite easily by measuring the weight difference between a membrane in the wet and dry state. To determine the

water content of a membrane, a sample is equilibrated in a test solution. After removing the surface water from the sample, the wet weight of the swollen membrane is determined. The sample is then dried at elevated temperature over phosphorus pentoxide under reduced pressure until a constant weight is obtained. The water content of a membrane is obtained in weight percent by:

$$\text{wt\% swelling} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100 \quad (2)$$

Here W_{wet} and W_{dry} are the weight of a membrane sample in the wet and the dry state.

Membrane Separation Properties Determined by Filtration Test

Both micro- and ultrafiltration are pressure-driven membrane processes using porous membranes. The separation of various components is based on a sieving mechanism, i.e., this membrane retains particles or molecules that are larger in size than the pores of a membrane. A relation as a function of the particle size and the pore size for the membrane retention can be defined by a relation between the pore and the particle radius (Ferry 1936). If the particles are spherical and have a radius r_s and the membrane pores are cylindrical with a radius r_p , the following relation can be applied to describe the membrane solute rejection:

$$R = \left[1 - \left(1 - \frac{r_s^2}{r_p^2} \right) \right]^2 \quad (3)$$

For the radius of the molecule, either the radius of gyration or the hydrodynamic radius can be used. The Ferry model is rather simplified, but gives a good approximation of the expected retention when particle size and the membrane pore radius are known.

Retention and Molecular Weight Cutoff

To describe the retention of ultrafiltration membranes, usually the molecular weight cutoff is used. The molecular weight cutoff determination is very sensitive to the experimental conditions, i.e., the solutes and their concentration used in the test, the applied pressure, and the temperature. Therefore, a comparison of retention data given by different manufacturers is generally problematic. As test conditions for determining the ultrafiltration membrane cutoff, a transmembrane pressure of 100 kPa, a feed solution concentration of 0.1 %, and a test temperature of 25 °C are recommended. Furthermore, a maximum of agitation of the feed solution at the membrane surface is required to minimize concentration polarization effects, and small amounts of solution should be filtered to assure a constant feed concentration.

The retention is generally expressed in % and defined by:

$$R = \left(1 - \frac{C_p}{C_f} 100 \right) \quad (4)$$

Here R is the retention or rejection of a membrane and C_f and C_p are the feed and the permeate concentration.

The retention of molecules having identical molecular weights may be rather different when their shape is different. Globular proteins, e.g., are rejected easier than branched polysaccharides or flexible polymers (Porter 1979). Adsorption of the solute to the membrane surface, e.g., might result in high “apparent” retention values when

the experiment is performed for a very short time period. Accumulation of solutes at the membrane surface due to concentration polarization effects can also obscure the retention measurements and must be considered when the true, i.e., intrinsic, retention shall be determined. Using low pressures, low feed concentrations, and a high degree of agitation can more or less eliminate these effects.

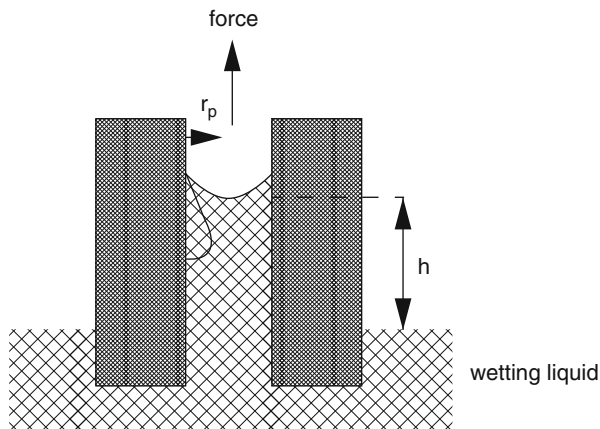
Manufactures of ultrafiltration membranes generally make use of marker molecules, e.g., dextrans and proteins, for the determination of the molecular weight cutoff value of their membranes. In addition to the molecular weight cutoff of a membrane, the sharpness of the cutoff is important for the practical application. The sharpness of the cutoff of a membrane is determined by measuring the retention of the membrane for components of different molecular weights and plotting the retention versus the molecular weight of the retained components. The sharpness of the cutoff of a membrane depends mainly on the pore size distribution of the membrane. For practical applications, the cutoff of a membrane should be as sharp as possible.

The Bacterial Challenge Test

Micro- and ultrafiltration membranes are often used in the food and pharmaceutical industry for the sterilization of solutions. In this application, it is important that membranes retain undesired microorganisms as completely as possible, i.e., the retention for microorganisms should be close to 100 %. Therefore, these membranes are exposed to a bacterial challenge test. In this test, the membrane is challenged with a solution containing a minimum concentration of organisms such as *Pseudomonas diminuta* per cm³ of solution (Cheryan 1998). The data obtained in bacterial challenge tests are normally expressed in terms of the log reduction value, which is given by the logarithms of the ratio of feed to filtrate concentration. The bacterial challenge test is a destructive test and is therefore not suited as an on-line quality control test. For this application, the nondestructive diffusion test and the bubble point integrity test are generally applied.

Characterization of Porous and Dense Membranes,

Fig. 3 Schematic drawing that illustrates the capillary effect of a membrane pore



Membrane Properties Determined by Membrane Pore Size Measurement

In addition to filtration tests, micro- and ultrafiltration membranes are characterized by determining their pore size and pore size distribution. A number of techniques such as liquid/gas and liquid/liquid displacement, mercury intrusion, permporosimetry, thermoporosimetry, etc. are used for the determination of the membrane pore size and pore size distribution. One of the more simple methods is the so-called bubble point test.

The Bubble Point Test

The bubble point test is a structure integrity test in which the largest pore or hole in a membrane is determined. The bubble point method is based on the capillary effect of small pores due to surface tension forces. In equilibrium these forces are balanced with gravity of the liquid in the pores. The principle is shown in Fig. 3.

This equilibrium between surface tension forces and gravity of the liquid in the pore can be expressed by the following equation:

$$2\pi r_p \sigma \cos \phi = r_p^2 \pi h \rho g \quad (5)$$

Here r_p is the pore radius, σ is the surface tension of the liquid in contact with air, $\cos \phi$ is the contact angle between the liquid and the wall of the pore, h is the height of the liquid column, ρ is liquid density, and g the acceleration of gravity.

The term $h \rho g$ in Eq. 5 can be replaced by the pressure p . This results in the Laplace equation, which is given by:

$$r_p = \frac{2\sigma \cos \phi}{p} \quad (6)$$

The bubble point method is a fairly simple technique where the pores of a membrane are filled with a liquid. From the bottom side of the membrane, nitrogen gas or air is introduced with increasing pressure. At a certain pressure, the gas will replace liquid in the largest pores permeating the membrane, and a bubble rising from the membrane surface can be observed.

Equation 6 referred to as Laplace equation gives a relation for the surface tension between the liquid and the gas and the required pressure to open up pores of a certain size. In the bubble point test, mostly water or isopropanol is used, since the surface tension of water/air is approximately 3.5 times higher than for isopropanol/air.

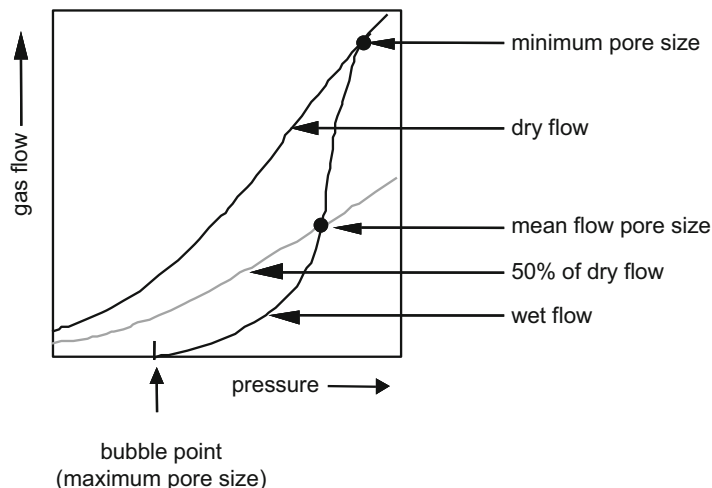
Other techniques to determine the pore size and pore size distribution of a porous membrane that are also based on the Laplace equation, but cover different pore size ranges when the same pressure range is applied, are mercury porosimetry, gas-liquid displacement, and liquid-liquid displacement.

The Mercury Porosimetry

In mercury porosimetry, a dry membrane is exposed to a certain volume of liquid mercury.

Characterization of Porous and Dense Membranes,

Fig. 4 Schematic drawing illustrating the gas/liquid displacement measurement to determine the pore size and pore size distribution of microfiltration membranes



The pressure applied to the mercury is slowly increased, while simultaneously the amount of mercury forced into the porous structure is measured. The largest pores will be filled first and the required pressure for the mercury to penetrate the porous structure increases with decreasing pore size. The required pressure corresponds to a certain pore radius and the amount of mercury that disappears in the membrane corresponds to the total volume of these pores. The interfacial tension of mercury and air is very high. Therefore, relatively high pressures are required to fill small pores. In polymer membranes, only pores having a radius in excess of 1 μm can be detected reliably by mercury porosimetry. Furthermore, this technique does not give distinction between dead-end pores and interconnected pores.

Gas-Liquid Displacement

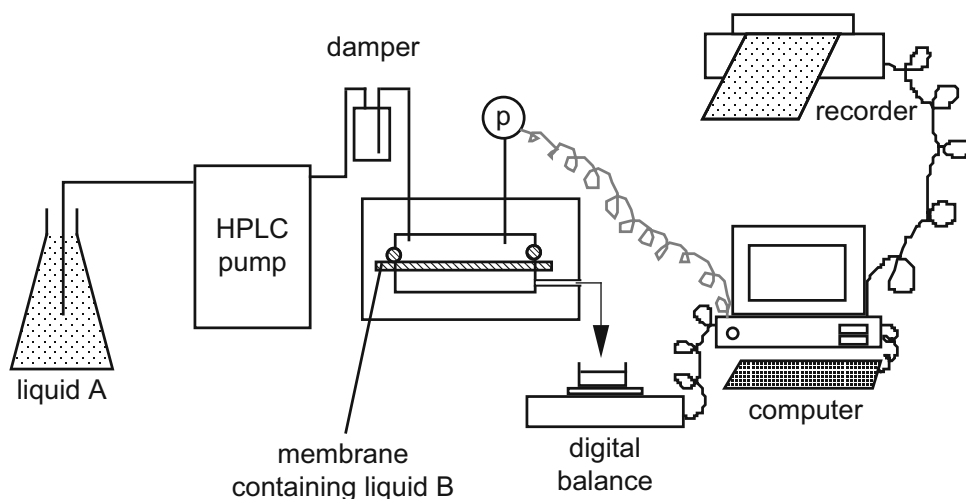
The gas-liquid displacement technique is identical to the bubble point method. The pores of the membrane are generally filled with an organic solvent which has a lower surface tension than water. The solvent is forced out of the membrane pores by nitrogen gas, which is introduced with increasing pressure. As the pressure increases, the liquid will be replaced by nitrogen in the largest pores first, and a convective gas flow through these pores will occur. The gas flow is measured as a function of the applied pressure. When all the pores are opened, a linear relationship between

pressure and gas flow is observed when the pressure is further increased. Figure 4 shows schematically typical gas fluxes obtained as a function of pressure with a dry and a liquid-filled membrane.

The mean flow pore size is given by the point where the 50 % “dry” flow curve crosses the “wet” flow curve. The maximum pore size is given by the point where a first flow through the liquid-filled membrane is observed. The minimum pore size is given by the point where the fluxes of the dry and the liquid-filled membrane become identical. The Laplace equation describes the relationship between the pore radius and the applied pressure.

Liquid-Liquid Displacement

Liquid-liquid displacement differs from gas-liquid displacement in the displacing medium; a second liquid instead of a gas displaces the liquid inside the pores. The two liquids applied should be immiscible. A typical liquid pair used is water/isobutanol. Both liquids are first saturated with each other before one of the liquids is used to fill the pores and the other liquid is applied as replacement liquid. The experimental setup for the determination of pore sizes by liquid-liquid displacement is shown in Fig. 5. A slow increase the replacement liquid pressure pushes the liquid out of the largest pores first. With increasing in pressure, the liquid in the smaller pores will also be replaced. The pore size distribution can be



Characterization of Porous and Dense Membranes, Fig. 5 Schematic representation of a typical liquid-liquid displacement setup (Capannelli et al. 1983)

calculated from a plot of the flux versus the applied pressure (Capannelli et al. 1983; Wienk et al. 1994).

Whether isobutanol or water is used as displacing liquid depends very much on the nature of the membrane material. Due to swelling phenomena, different results might be obtained depending on the liquid placed inside the pores.

The relation between the pore radius and the pressure required to open pores of a certain size is again described by the Laplace equation, and the pore size distribution can now be calculated when the flux as a function of the pressure is measured.

Like in gas-liquid displacement, only active pores contributing to transport are taken into account. Pore diameters of approximately 5–100 nm can be analyzed using liquid-liquid displacement. The advantage of liquid-liquid displacement over gas-liquid displacement is the lower interfacial tension between liquid pairs compared to a gas/liquid pair. Therefore, pores of the same size can be opened at much lower pressures in liquid-liquid displacement.

There are more methods that can be used to determine pore sizes in porous membranes (Cuperus et al. 1992a, b) such as permoporometry or thermoporometry, which is based on the microcalorimetric analysis of a solid-liquid transition

using a sensitive differential scanning calorimetry. Permoporometry is a technique based on gas adsorption/desorption measurements where pores are either filled by controlled condensation of a vapor phase or where filled pores are emptied by controlled evaporation of the liquid inside the pores. The relation between the relative vapor pressure and the pore radius is given by the Kelvin equation. Thermoporometry is based on the microcalorimetric analysis of a solid-liquid transition using a sensitive differential scanning calorimetry.

Table 1 shows the pressures required to open pores of 10 nm for different displacement systems. A second advantage is that membranes are characterized in a wetted state, and therefore the test conditions are closer to the real operating conditions.

Dense Membrane Characterization

Dense membranes are generally used for the separation of low molecular mass materials such as gases, salts, or solvents. The transport mechanism in these membranes is based on the solution and diffusion of components within the membrane matrix. The intrinsic properties of the basic membrane material are often more relevant for

Characterization of Porous and Dense Membranes,**Table 1** Different porosimetry techniques and the influence of the interfacial tension on the pressure required opening pores of 10 nm

Technique	System	Pressure	
		(mN/m)	(Bar)
Mercury porosimetry (G-L)	Air/mercury	480	749
Bubble point (G-L)	Air/water	72.3	145
Coulter porometry (G-L)	Air/Porofil®	16	32
Gas-liquid displacement (G-L)	Air/isobutanol	20.7	41
Liquid-liquid displacement (L-L)	Water/isobutanol	1.85	3.7
Liquid-liquid displacement (L-L)	Water/isobutanol/methanol	0.35	0.7

characterizing their transport behavior than is the macroscopic membrane structure. Characterization methods used with microporous structures have therefore been supplemented with other procedures, such as sorption and diffusion measurements or determination of the glass transition temperature and crystallinity of the basic membrane material. For ion-exchange membranes, the measurement of electrokinetic properties is required.

In addition to the determination of diffusion and partition (solubility) coefficients, measurements providing information on the physical structure of the polymer, such as differential scanning calorimetry, X-ray studies, or determination of the free volume in a polymer, are important. These methods are described in Koros and Chem (1987), Berens and Hopfenberg (1982), and Morel and Paul (1982). Permeability and selectivity are the most interesting parameters; they are determined in permeation tests and expressed in terms of rejection coefficients (in reverse osmosis) or separation coefficients (in gas separation and pervaporation). These coefficients are usually not constant but a function of composition, temperature, and pressure. Furthermore, boundary layer effects at the membrane surface often obscure the determination of membrane fluxes and selectivities in practical measurements.

The methods used to determine the structural properties of ion-exchange membranes are similar to those used for characterizing other polymer membranes. Because ion-exchange membranes are used mainly in separation processes with electrical potential driving forces, their permeability and selectivity are determined under experimental conditions closely related to their practical use, and their properties are expressed in terms commonly used in electrochemistry (e.g., electrical resistance, ion-transfer numbers, charge densities) (Cussler 1971, 1984).

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Charged Mosaic Membrane

► Mosaic Membranes

Charged Ultrafiltration Membrane

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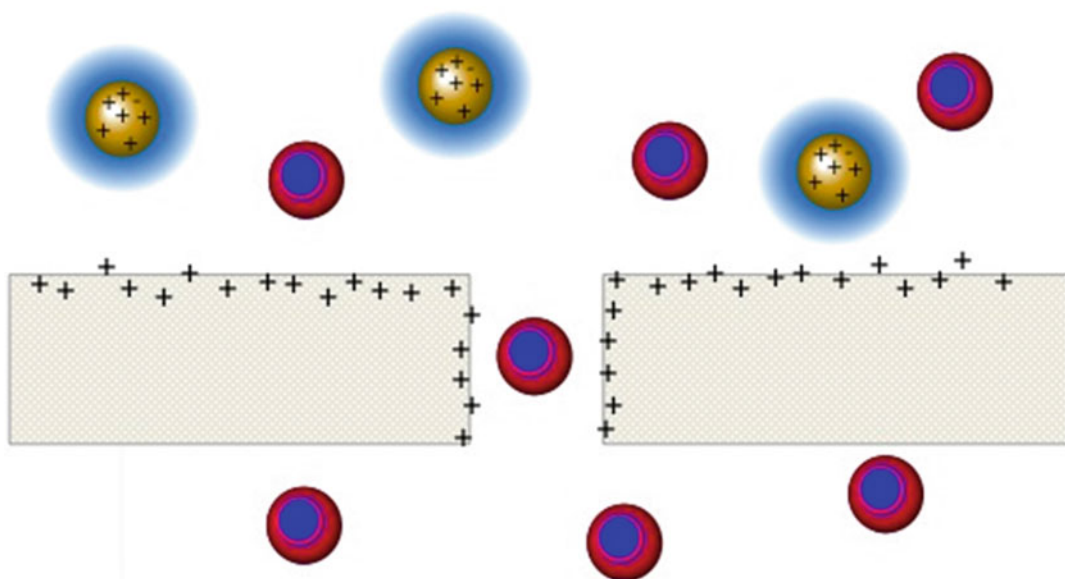
Electrically charged ultrafiltration membranes can be used to reduce the fouling and increase the retention of like-charged species. Most polymeric membranes have a net negative charge in solution due to the presence of trace anionic groups (e.g., carboxylic acids) and/or the preferential adsorption of negatively charged ions from the aqueous solution. It is also possible to cast membranes from polymers containing fixed charge groups, e.g., a positively charged membrane can be developed using polymers containing fixed amine groups. However, the most common method for generating charged ultrafiltration membranes is by surface modification of a base polymer through the attachment of appropriate anionic (e.g., carboxylic or sulfonic acid) or cationic (e.g., quaternary amine) groups. The overall performance of these membranes is determined by the density of the charge

groups, the chemistry of the ligand and the covalent linkage, and the properties of the spacer arm used to attach the ligand to the membrane (Zydney 2011).

One of the first applications of charged ultrafiltration membranes was in the recovery of electropaint. Electrodeposition of a charged paint resin is used extensively in the industrial painting of metallic surfaces in automobiles and large household appliances. The paint resins are organic polymers with attached anionic or cationic groups. Ultrafiltration has been used to recover the charged electropaint from the dilute solution produced by washing the excess paint off of the metal part. Ultrafiltration can also be applied directly to the paint in the electrodeposition bath, with the permeate (essentially water) used for subsequent rinsing steps (Zeman and Zydney 1996). The use of charged membranes (having the same polarity as the electropaint) provides significantly greater filtrate flux with less fouling than neutral or oppositely charged membranes.

Charged ultrafiltration membranes can be used to significantly improve the inherent tradeoff between the permeability and selectivity of an ultrafiltration membrane (Mehta and Zydney 2005). The rate of solute transport through a charged ultrafiltration membrane is determined by a combination of steric (size based) and electrostatic interactions (Mehta and Zydney 2006). Electrostatic interactions strongly effect the partitioning of charged solutes into the membrane pores. For example, the presence of positively charged groups on the pore surface causes a strong electrostatic exclusion of positively charged species from the membrane pores significantly increasing the selectivity of the membrane. This makes it possible to employ charged ultrafiltration membranes with relatively large pore size and thus with very high permeability, with the required selectivity achieved by electrostatic exclusion of the protein.

There is also considerable interest in performing protein separations by charged UF membranes. In this case, the charged ultrafiltration membrane provides very high retention of like-charged proteins, enabling uncharged proteins and smaller impurities to be washed into the permeate by a diafiltration process (see Fig. 1). The solution pH and ionic strength can be adjusted to obtain high-resolution



Charged Ultrafiltration Membrane, Fig. 1 Positively charged membrane provides high retention of positively charged protein while allowing transmission of neutral proteins

protein separations (van Reis et al. 1999). Van Reis and Zydney (2007) have discussed a number of separation processes using charged ultrafiltration membranes, including a nonaffinity process for purifying a monoclonal antibody from harvested cell culture fluid.

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Chemical and Electrochemical Equilibrium in Membrane Systems

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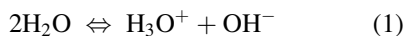
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Equilibrium in a system is achieved when all components are in the same thermodynamic state, i.e., the Gibb's free energy of the system is constant. Equilibrium between two systems such as a membrane and an adjacent solution or two solutions separated by a membrane is obtained when both

systems are in the same thermodynamic state, i.e., when the Gibb's free energies in both systems are identical. The Gibb's free energy of a system is a function of various state variables such as pressure, electrical potential, and the activity of individual components. A system composed of water and an electrolyte which is partially dissociated will be in equilibrium when dissociated and non-dissociated components are in equilibrium. Considering two systems separated by a membrane which is impermeable to some components and permeable to others, the two systems will be in equilibrium when all components that are able to permeate the membrane have identical electrochemical potentials in both systems. This may also be the case if the components do have differences in pressures, electrical potentials, or the activities in the two systems as long as these differences compensate each other and the sum of the state variables, i.e., the Gibb's free energy in both systems is identical. Examples for two systems being in equilibrium are the osmotic equilibrium, in which pressure and activity differences compensate each other, and the Donnan equilibrium which is obtained when an electrical potential difference is compensated by activity difference. For membrane processes, the dissociation equilibrium in a system as well as the osmotic and the Donnan equilibrium between two systems are of importance and will be discussed in more detail.

Water is dissociated to a certain extent into hydronium and hydroxide ions, i.e., H_3O^+ and OH^- ions according to the following equilibrium relation:



The water dissociation equilibrium constant K is

$$\frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} = K \quad (2)$$

The brackets $[\]$ denote concentrations of the various components in equilibrium.

In pure water, the concentration of water is 55.6 mol L^{-1} . The product of $K \times [\text{H}_2\text{O}]^2$ is constant and referred to as the water dissociation

product K_w which is $1.008 \times 10^{-14} [\text{mol}^2 \text{L}^{-2}]$ at 25°C (Atkins 1990). It is

$$\begin{aligned} [\text{H}_3\text{O}^+][\text{OH}^-] &= K [\text{H}_2\text{O}]^2 = K_w \\ &= 10^{-14} \text{ (at } 25^\circ\text{C)} \end{aligned} \quad (3)$$

The K_w value is a function of temperature. However, at constant temperature and in electrolyte solutions with low to moderate ion concentrations, the water concentration does not change very much and K_w can be considered constant, and in pure water, the concentrations of H_3O^+ and OH^- ions are identical and are $10^{-7} [\text{mol L}^{-1}]$ at 25°C .

In electrolyte solutions containing an acid or a base, the concentrations of H_3O^+ and OH^- ions are no longer identical, and their concentrations are expressed by the so-called pH value (*potentia hydrogenii*). The pH value is defined as the negative logarithm of the H_3O^+ -ion concentration to the basis of 10. Thus, is

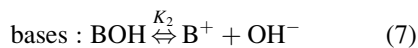
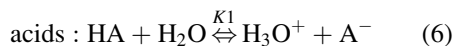
$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} \quad (4)$$

and

$$[\text{OH}^-] = 10^{-(14-\text{pH})} \quad (5)$$

Pure water or neutral electrolyte solutions at 25°C have a pH value of ca 7. Acid exhibits pH values <7 and bases >7 .

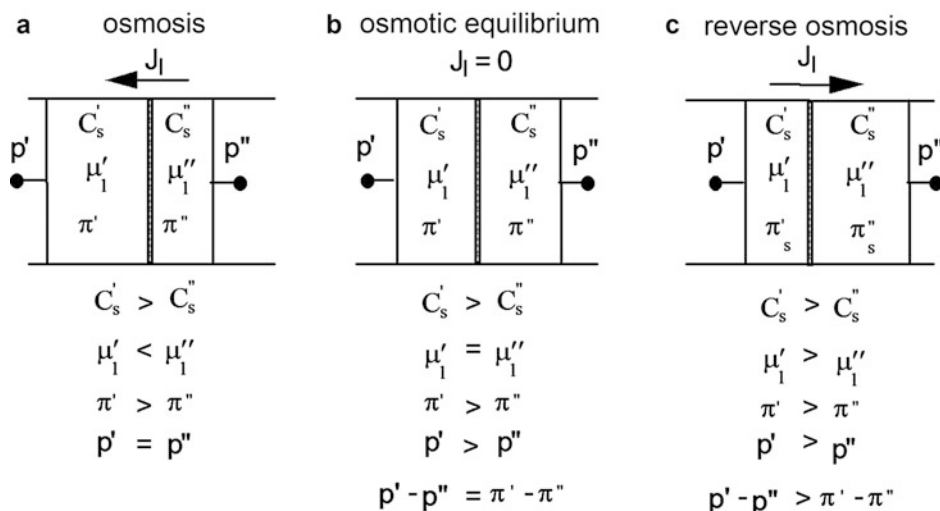
An important parameter for acids and bases is the dissociation constant expressed in the so-called pK value. The dissociation of acids and bases follows the general scheme:



Here, K_1 and K_2 are the dissociation equilibrium constants, and HA and BOH represent the non-dissociated acid and base.

The acid and base equilibrium can be expressed by the following relations:

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_1[\text{H}_2\text{O}] = K_a \quad (8)$$



Chemical and Electrochemical Equilibrium in Membrane Systems, Fig. 1 Schematic drawing illustrating the osmotic phenomenon. It shows two systems (') and (') separated by a semipermeable membrane. The

phases consist of a solvent and a solute indicated by the subscripts l and s . C and μ refer to concentration and chemical potential, p to hydrostatic, and π to osmotic pressure, respectively, and J to the membrane flux

and

$$\frac{[B^+][OH^-]}{[BOH]} = K_2 = K_b \quad (9)$$

Here, K_a and K_b are the dissociation constants for the acid and the base.

The dissociation constant between strong and weak acids or bases can vary by several orders of magnitude. Therefore, the dissociation constant is generally expressed by the so-called pK_a and pK_b values which are defined similarly to the pH value as the negative logarithm of the dissociation constant, i.e.,

$$pK_a = -\log K_a = 10^{-pK_a} \quad (10)$$

and

$$pK_b = -\log K_b = 10^{-pK_b} \quad (11)$$

Multivalent acids or bases such as H_2SO_4 or $Ca(OH)_2$ which have more than one dissociable proton or hydroxide ion dissociate in consecutive steps and, therefore, have more than one pK_a or pK_b value, respectively.

In practical applications the degree of dissociation of an electrolyte is of interest. It is defined as the ratio of dissociated molecules to the total

number of molecules present in a solution and given by:

$$\alpha = \frac{[A^-]}{v_{A'}[AB] + [A^-]} = \frac{[B^+]}{v_{B'}[AB] + [B^+]} \quad (12)$$

Here, α is the dissociation degree and AB is the total concentration of the non-dissociated electrolyte. A^- and B^+ are anion and cation concentrations.

The degree of dissociation α has values between 1 for a totally dissociated electrolyte and 0 for a completely non-dissociated electrolyte.

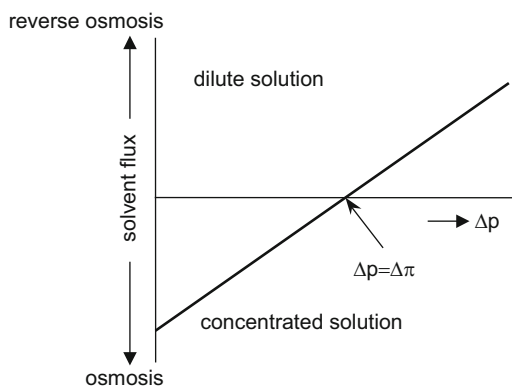
From practical experience, it is well known that the degree of dissociation of weak acids or bases depends on the pH value of the solution. In solutions with high pH values, weak acids have a higher degree of dissociation than in solutions with low pH values.

If two aqueous salt solutions of different concentrations are separated by a membrane which is permeable for the solvent, e.g., water, but impermeable for the solute, e.g., salt, a transport of water from the more dilute solution in the more concentrated solution is observed. This phenomenon, which is illustrated in Fig. 1, is referred to as osmosis.

The figure shows a schematic diagram of a membrane separating two solutions consisting of a solvent, e.g., water, and a solute, e.g., a salt. The two solutions are indicated by (') and ("). The membrane is assumed to be permeable to the solvent but impermeable to the solute. Depending on the concentrations and hydrostatic pressures in the two phases separated by the membrane, four different situations can be distinguished:

- The hydrostatic pressures in the two phases separated by the membrane are equal, but the solute concentration in solution (') is higher than the one in solution ("). In this case, the osmotic pressure in solution (') is higher than that in solution ("), and there will be a flow of solvent from the more diluted solution (") into the more concentrated solution ('). This situation is referred to as *osmosis*.
- The two phases separated by the membrane have different hydrostatic pressures, but the difference in hydrostatic pressure is equal to the difference in the osmotic pressures between the two solutions acting in opposite direction. This situation is referred to as *osmotic equilibrium*, and there will be no flow of solvent through the membrane, although the concentrations in the two solutions are different.
- The two phases separated by the membrane have different hydrostatic pressures, but the difference in hydrostatic pressure across the membrane is larger than that in the osmotic pressure and is acting in opposite direction. Thus, solvent will flow through the membrane from the solution (') with the higher solute concentration into the solution (") with the lower solute concentration. This phenomenon is referred to as *reverse osmosis*.

The flux of solvent between two homogeneous solutions of different concentrations separated by a semipermeable membrane, which is only permeable for the solvent, to the more concentrated solution as a function of a hydrostatic pressure applied is illustrated in Fig. 2. Here, the solvent flux between two solutions of different concentrations through a strictly semipermeable membrane



Chemical and Electrochemical Equilibrium in Membrane Systems, Fig. 2 Solvent flux between two solutions of different concentrations through a strictly semipermeable membrane as function of the hydrostatic pressure applied to the more concentrated solution

is shown as a function of the hydrostatic pressure applied to the more concentrated solution.

As long as the applied hydrostatic pressure is lower than the osmotic pressure, the difference between the two solutions' solvent will flow from the more dilute solution into the more concentrated solution by osmosis. When the hydrostatic pressure exceeds the osmotic pressure difference, the flow is reversed and solvent will flow from the more concentrated solution to the dilute solution.

The osmotic pressure of a solution π is proportional to the solute concentration. It can be calculated, however, from the activity of the solvent in a solution and is given by:

$$P^S - P^l = \pi = \frac{RT}{V_l} \ln a_l^s \quad (13)$$

For dilute solutions, the osmotic pressure can be expressed to a first approximation by the concentration of the individual components in the solution (Strathmann 2004):

$$\pi = RT \sum_i g_i C_i \quad (14)$$

If the solute is a salt, as is the case in many practical applications, the concentration of the individual ions must be considered when

determining the osmotic pressure, i.e., the degree of dissociation, and the stoichiometric coefficients of the salt have to be considered for determining the osmotic pressure.

The osmotic pressure of an aqueous solution with salts is given by (Robinson and Stokes 1959):

$$\pi = RT \sum_i g_i (v_{ic} + v_{ia}) C_{is} \quad (15)$$

Here, g is the osmotic coefficient; the subscripts v , c , and a refer to a stoichiometric coefficient, cation, and anion.

In discussing the osmotic pressure, it was assumed that two solutions separated by a membrane are in chemical equilibrium. If the solution contains charged components, i.e., ions, and the membrane is permeable for at least one ionic component, the membrane will be in equilibrium with the adjacent solution if the electrochemical potential of all ions in the membrane and the solution are equal. Thus, for each ion in equilibrium, it is

$$\tilde{\mu}_i^m = \tilde{\mu}_i^s = \mu_i^m + z_i F \varphi^m = \mu_i^s + z_i F \varphi^s \quad (16)$$

Here, μ_i and $\tilde{\mu}_i$ are the chemical and the electrochemical potential of the component i , φ is the electrical potential, and F is the Faraday constant. The superscripts m and s refer to the membrane and to the solution, respectively.

Thus, the electrochemical potential of an ion is composed of two additive terms. The first is the chemical potential and the second is the electrical potential multiplied by the Faraday constant and the valence of the ion. Introducing the chemical potential $\mu_i (d\mu_i = \bar{V} dp_i + RT d \ln a_i)$ into Eq. 16 and rearranging gives the electrical potential difference between the membrane and the adjacent solution (Donnan and Guggenheim 1932) to

$$\varphi^m - \varphi^s = \frac{1}{z_i F} \left[RT \ln \frac{a_i^s}{a_i^m} + \bar{V} (p^s - p^m) \right] = \varphi_{Don} \quad (17)$$

Here, φ is the electrical potential, a is the ion activity, $\bar{V}$ is the partial molar volume, z is the valence, F is the Faraday constant, p is the pressure, T is the absolute temperature, and R is the gas

constant; the subscript i refers to individual components and the superscripts m and s refer to the membrane and the electrolyte solution, respectively. The potential difference between the membrane and the solution is referred to as Donnan potential φ_{Don} .

The Donnan potential between an electrolyte solution and an ion exchange membrane cannot be measured directly. It can, however, be calculated from the ion activities in the solution and the membrane and by the pressure difference between the membrane phase and the adjacent solution, $p^m - p^s$, which is referred to as swelling pressure and which is identical to the osmotic pressure difference between the solution and the membrane.

Introducing the osmotic pressure into Eq. 17 gives the Donnan potential as a function of the ion and the water activities in the membrane and the solution:

$$\varphi_{Don} = \frac{1}{z_i F} \left[RT \ln \frac{a_i^s}{a_i^m} - \bar{V}_i \Delta \pi \right] \quad (18)$$

The numerical value of the Donnan potential φ_{don} can be calculated either from the cation or anion activities. For a single salt, thus is

$$\begin{aligned} \varphi_{Don} &= \frac{1}{z_c F} \left[RT \ln \frac{a_c^s}{a_c^m} - \bar{V}_c \Delta \pi \right] \\ &= \frac{1}{z_a F} \left[RT \ln \frac{a_a^s}{a_a^m} - \bar{V}_a \Delta \pi \right] \end{aligned} \quad (19)$$

Equation 19 gives a general relation for the cation and anion distribution at the interface between a solution and an ion exchange membrane.

It should be noted that the value of the Donnan potential is negative for the cation exchange membrane and positive for the anion exchange membrane in equilibrium with a dilute electrolyte solution.

The Donnan equilibrium describes the electrochemical equilibrium of an ion in an ion exchange membrane, and an adjacent solution and can be calculated for a single electrolyte by rearranging Eq. 19:

$$\left(\frac{a_a^s}{a_a^m} \right)^{\frac{1}{z_a}} \left(\frac{a_c^m}{a_c^s} \right)^{\frac{1}{z_c}} = e^{-\frac{\Delta \pi \bar{V}_s}{RT z_c v_c}} \quad (20)$$

Here, z is the valence, ν is the stoichiometric coefficient of the electrolyte, F is the Faraday constant, R is the gas constant, T is the absolute temperature, $\bar{V}$ is the partial molar volume, and a is the activity; the subscripts a and c refer to anion and cation, and the superscripts s and m refer to the solution and the membrane, respectively.

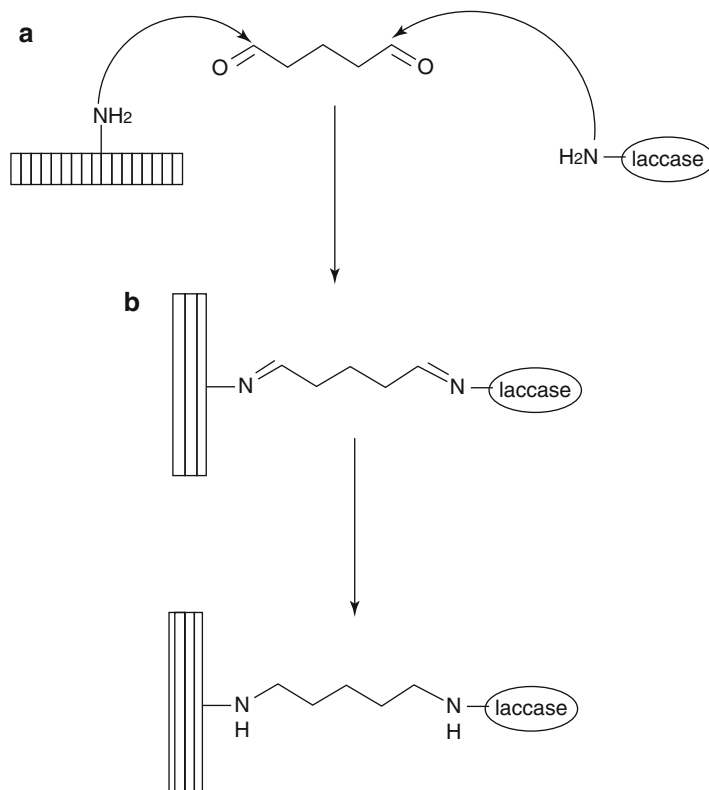
The Donnan equilibrium is an important relation in electro-membrane processes since it determines the distribution of co- and counterions between the membrane and the adjacent solution.

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Chemical Binding of Biomolecules to Membranes,

Fig. 2 Laccase immobilization on modified electrode with polyaminopyrrole; (a) nucleophilic attack on the glutaraldehyde, (b) reduction of imine function (IEM picture)

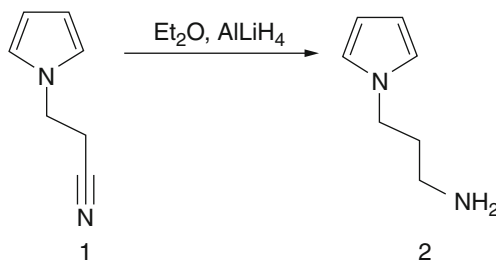


Chemical Binding of Biomolecules to Membranes

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The immobilization in electropolymerized polymers such as polypyrrole has been developed for a variety of biomolecules and provides



Chemical Binding of Biomolecules to Membranes, Fig. 1 Scheme of synthesis of amino propyl pyrrole

very stable environment for the biocatalyst. The advantages of the polypyrrole are the control of film thickness and its contribution in electron transfer between the biocatalysts and the conductive support.

Amino pyrrole is synthesized according the following scheme (Fig. 1).

Electropolymerization of 1-(2-cyanoethyl)pyrrole monomer (1) in acetonitrile 0.1 M NBu_4PF_6 was performed by controlled-potential oxidation of the pyrrole at +1.01 V vs. SCE. Reduction of the nitrile to amine function was carried out using a large excess of LiAlH_4 in dried ether at room temperature.

Enzyme is grafted on the modified tube (with amino polypyrrole) by using glutaraldehyde as coupling agent (Fig. 2).

Fixation of laccase (enzyme which catalyzed the oxygen reduction) on the modified electrode has been investigated and applied to the fabrication of biocathode for enzymatic biofuel cell (Servat et al. 2007).

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Chemical Cleaning of Membranes

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Introduction

Cleaning of membranes is carried out to enhance its permeability followed by performance in a membrane-based treatment plant. The Pareto principle – 80/20 rule – that 80 % of effects result from 20 % of the causes best describes the discussion, where membrane fouling is the cause (the 20 %) and cleaning is the effect (the 80 %).

Fouling in membrane filtration is problematic but inevitable as it occurs with the retention of contaminants that accumulate on the membrane surface. The causes of fouling are often specific, depending upon feed water constituents, the membrane, and the operating regime. Cleaning protocols are typically recommended by the membrane manufacturers with some cleaners being proprietary. We can minimize the rate of fouling, but we cannot eliminate fouling, unless very extensive pretreatment is applied. Types of fouling are presented along with cleaning, physical and chemical conditions that have significant impacts on cleaning efficiency, and compatibility of membrane materials with cleaning agents.

Membrane fouling is a complicated phenomenon and results from numerous causes. In spite of its complexity, electrostatic and hydrophobic/hydrophilic interactions that involve both membrane and fouling materials are recognized to have significant bearing. This is especially for more-difficult-to-clean membrane fouling dominated by natural organic matter (NOM) and microbes. Membrane fouling is referred to the flux decline of a membrane filter caused by the accumulation of certain constituents in the feed on the surface of the membrane or in membrane matrix. Certain fouling materials can be removed hydraulically (backwash or scrubbing); however, most can be removed by chemical means such as clean-in-place (CIP) or chemical cleaning.

The technique of investigating a fouled membrane – “membrane autopsy” – identifies the cause of poor membrane performance and hence gives the opportunity to rectify or mitigate the problem and improve future plant design.

Membrane Fouling and Chemical Cleaning

Chemical cleaning is an integral part of membrane process operation that has a marked effect on the performance and economics of the process. A decline in RO membrane performance can be caused by fouling (organic and inorganic fouling and biofouling), operational mishaps, and

membrane element quality. The behavior and frequency of RO system fouling are affected by feed water source and quality, pretreatment requirements, pretreatment chemicals, and system design and operation. During normal operation over a period of time, RO membrane elements are subject to fouling by suspended or sparingly soluble materials in the feed water. According to the type of foulants, five categories of membrane fouling are presented.

- Inorganic fouling/scaling
- Particle/colloid fouling
- Biological fouling (bacterial bioslime, algae, mold, or fungi)
- Organic fouling
- Sulfate scale of calcium, barium, or strontium

Generally RO membrane suppliers recommend membrane cleaning when:

- Normalized permeate flow declines by 10 %
- Pressure drop declines by 10 %
- Normalized salt passage increases by 10 %

Well-designed, well-operated RO systems are usually cleaned one to four times per year. Irreversible membrane element performance decline such as membrane compaction and intrusion contributes to the 0.7 flow factor. Based on this permeate flow profile, the system's stabilized performance is a flow factor of 0.7. Cleaning criteria should be based on actual stabilized membrane element performance. The typical cleaning criteria (10 % normalized permeate flow decline or 0.9 flow factor) are not applicable, because true membrane element performance is a permeate flow factor of 0.7. Cleaning performed at a 0.7 flow factor has no effect but increases the OPEX (operating expenses).

Therefore, RO system cleaning criteria must be customized to actual stabilized element performance. The criteria can be customized to site conditions. For instance, calcium carbonate is a foulant that can be easily and effectively removed with a hydrochloric acid solution at pH 2. For sites with low energy costs, cleaning may be carried out when the normalized permeate flow decline is 20 %.

For difficult-to-remove foulants – silicates and organics – cleaning should be performed when the normalized permeate flow decline is 10–15 %. In many cases, commercial membrane cleaners are required but they increase OPEX.

Inorganic Fouling/Scaling

Inorganic fouling or scaling is caused by the accumulation of inorganic precipitates such as metal hydroxides and “scales” on membrane surface or within pore structure. Precipitates are formed when the concentration of chemical species exceeds their saturation limits. Scaling is a major concern for reverse osmosis (RO) and nanofiltration (NF) membrane processes. RO and NF membranes reject inorganic species. These species, if allowed to build up, form a concentrated layer of concentration polarization. For microfiltration (MF) and ultrafiltration (UF), inorganic fouling due to concentration polarization is much less; however, they can exist due to interactions between ions and foulants (organic polymers) via chemical bonding. Coagulation and oxidation, if not designed or operated properly, might introduce metal hydroxides on membrane surface or within pore structure. Inorganic fouling and scaling can be a significant problem for makeup water of caustic solution used for chemical cleaning.

Particulate/Colloidal Fouling

Accumulation of particulate material (dirt, sand) on the membrane surface – plugging – leads to particulate fouling. Algae, bacteria, and certain natural organic matters fall into this category. However, they are different from inert particles and colloids such as silts and clays. In most cases, particles and colloids do not really foul the membrane because the flux decline is largely reversible by hydraulic cleaning measures such as backwash and air scrubbing.

Microbial/Biological Fouling

Microbial fouling is a result of formation of biofilms on the membrane surface. Once bacteria get attached to the membrane, they start to multiply and produce extracellular polymeric substances (EPS) to form a viscous, slimy, hydrated

gel. The severity of microbial fouling is intrinsically related to the quality of feed water like environmental conditions for microbial growth, availability of nutrients, and abundance of microbes. Organic-based deposits resulting from bacterial slimes, fungi, molds, etc. can be difficult to remove, if the feed is plugged. Plugging of the feed makes it difficult to introduce and distribute the cleaning solutions. To inhibit additional growth, it is important to clean and sanitize not only the RO system but also the pretreatment, piping, dead legs.

Bacteria present a significant fouling problem in most of the RO plants. As they grow and multiply, they normally produce biofilm, organic films of lipopolysaccharides, to encase and protect the bacteria. These biofilms cover the membrane surface resulting in fouling.



Chemical Cleaning of Membranes, Fig. 1 Fouled RO membrane

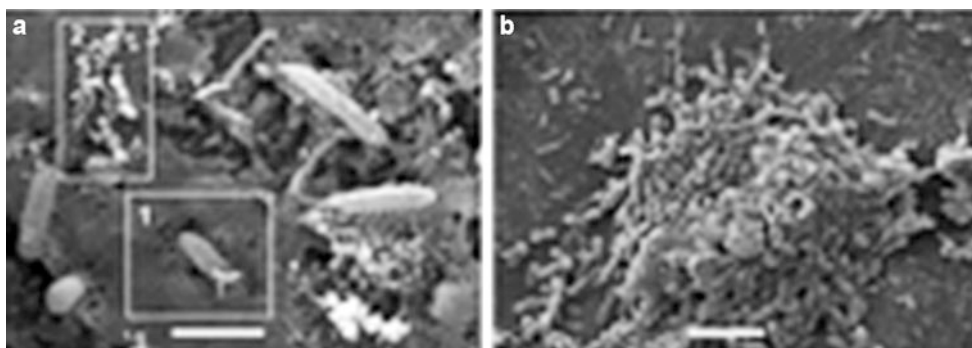
Figure 1 is a photograph of fouled reverse osmosis membranes. Deposits of silt are composed of suspended particulates of all types that accumulate on the membrane surface. Sources of silt are organic colloids, iron corrosion products, precipitated iron hydroxide, algae, and fine particulate matter. Silt density index (SDI) testing is a widely accepted method for estimating the rate at which colloidal and particle fouling will occur in water purification systems, especially using reverse osmosis (RO) or nanofiltration (NF) membranes.

Shown in Fig. 2 are scanning electron micrographs of the surface of the RO membrane after 4 and 16 days. (A) Rod-shaped gels embedded in an extracellular fibrillar material structure (square 1). Compact aggregates are visible on top of this biofilm (square 2). The RO membrane surface is visible at the bottom (under the biofilm layer) as a rough-appearing texture. (B) Typical microcolony formed on the surface of the membrane after 16 days (Fig. 3).

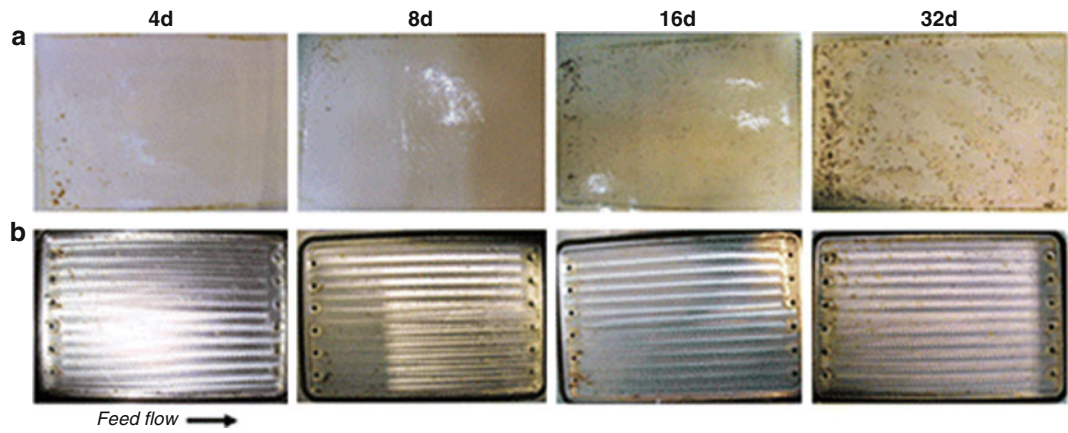
Shown above are series of photographs of fouled reverse osmosis membranes (A) and their feed-side spacers (B). The membranes and spacers were removed from the flow cells after 4 (column 4 d), 8 (column 8 d), 16 (column 16 d), and 32 (column 32 d) days of operation. The direction of the feed water flow along the length of each flow cell was from left to right.

Organic Fouling

Organic fouling is significant in membrane filtration with source water containing relatively high natural organic matters (NOM). Surface



Chemical Cleaning of Membranes, Fig. 2 SEM imaging of biofilms



Chemical Cleaning of Membranes, Fig. 3 Fouled membranes

Chemical Cleaning of Membranes, Table 1 Effects of operating strategies on fouling

Type of fouling	Hydraulic cleaning	Feed chlorination	Feed acidification	Chemical cleaning
Inorganic	—	—	++	++
Particulate	++	—	—	++
Microbial	+	++	+ ^a	++
Organic	—	+	—	++

—No effect or negative effects

+Some positive effects

++Always positive effect

^aIn conjunction with feed chlorination

water (lake, river) typically contains higher NOM than groundwaters, with exceptions. For source water high in NOM, organic fouling is the most significant factor in flux decline. NOM typically contains about 50 % humic substances. Some organic molecules (oils, greases, humic/fulvic acids, surfactants), occurring either naturally or synthetic, coat and plug the membrane pores.

The effects of various operating strategies against different types of fouling are summarized in Table 1. As indicated, chemical cleaning is the most effective strategy for all types of membrane fouling.

Chemical Cleaning of Silica Fouling

Chemicals for silica fouling control can be divided into three categories:

- Chemicals for silica inhibition
- Chemicals for silica dispersion (Neofotistou and Demadis 2004)
- Chemicals for silica scale removal from membrane surfaces

Silica inhibitors can retard the polymerization of silica, which exceeded its solubility, i.e., phosphonate-based chemicals. Dispersants can work by placing a surface charge on the polymerized silica and cause repulsion and dispersion of these polymerized structures into water phase (Dudley and Baker 1999).

Polymerization of dissolved silica (i.e., supersaturation and catalyzed by hardness) can be difficult to remove. This type of silica fouling is different from colloidal and particulate silica, which may be associated with either metal hydroxides or organic matter. It might be difficult to remove polymerized silica by typical

chemical cleaning process. However, polymerized silica scales removed with a high pH cleaning solution (pH of 10–11) were reported. Caustic (sodium hydroxide) at maximum pH allowed by the membrane manufacturer will remove polymerized silica scales but it will take many hours to remove a silica scale. Colloidal silica and particulate silica coating, not associated with either metal hydroxides or organic matter, can be removed from membrane surface by physical flushing.

MF and UF membranes can be of organic polymers or inorganic materials, whereas NF and RO membranes are all organic polymers only.

Membrane Cleaning Chemicals

Selection and Use of Cleaning Chemicals

The first time cleaning is performed, it is recommended to contact the manufacturer of the equipment, the RO element manufacturer, and service supplier. The cleaning chemicals can be generic or proprietary.

It is not unusual to use a number of different cleaning chemicals in a specific sequence to achieve optimum cleaning. A high pH cleaning is used to remove foulants like mineral scale or metal hydroxides/oxides. The order of high and low pH cleaning solution could be reversed or only one solution is required under the situation. Detergents are added to aid in the removal of heavy biological and organic matter, while other foulants need a chelating agent like EDTA for the removal of colloidal material, organic and biological material, and sulfate scale. An improper selection of cleaning chemical or the protocol thereof can make the entire cleaning exercise worse.

Iron deposits and scaling require a simple low pH cleaning. For most complex fouling, the sequence below may be followed:

- Flushing with permeate and with nonoxidizing biocide at the end of flushing
- High pH CIP (clean-in-place) with temperature versus pH
- Flushing with permeate till pH on the brine side <8.5

Chemical Cleaning of Membranes, Table 2 Categories of membrane cleaning chemicals

Category	Functions	Typical chemicals
Caustic	Hydrolysis, solubilization	NaOH
Oxidants/disinfectants	Oxidation, disinfection	NaOCl, H ₂ O ₂ , peroxyacetic acid
Acids	Solubilization	Citric acid, nitric acid
Chelating agents	Chelation	Citric acid, EDTA
Surfactants	Emulsifying, dispersion, surface conditioning	Surfactants, detergents (SDS, sodium dodecyl sulfate)

- Low pH CIP (clean-in-place)
- Acid flushing with permeate and nonoxidizing biocide

Once the cause of membrane fouling is identified, various cleaning chemicals can be used to remove foulants from the membrane and to restore the membrane flux. Chemicals commonly used for cleaning MF and UF membranes in water industry fall into five categories, as shown in Table 2.

Caustic

Caustic is used to clean membranes fouled by organic and microbial foulants. The function of caustic is twofold: (1) hydrolysis and (2) solubilization. There are a number of organic materials including polysaccharides, and proteins that can be hydrolyzed by caustic. Cellulose-based membranes based on polysaccharides hydrolyze; hence, such membranes are to be used in a limited pH range. This is due to the hydrolysis of cellulose – a simple polysaccharide – consisting of thousands of glucose linked by 1,4- β -glucoside bonds. Fats and oils also react with caustic through saponification, generating water-soluble soap micelles.

An important function of caustic is to increase negative charges of humic substances. Hence, they are easier to be removed from membranes. Humic substances contain functional groups that are organic acids. Their acidity ranges from pK_a (negative logarithm of the dissociation constant)

of 1.2 (oxalic) to 13 (phenol), with an average pK_a of 4.2 (Thurman 1985). During caustic cleaning, pH of cleaning solution can be as high as 13.

Acids and Chelating

Acids are used primarily for removing scales and metal dioxides from fouling layers. When membrane is fouled by iron oxides, citric acid is quite effective because it not only dissolves iron oxide precipitates but also forms complex with iron. The removal of divalent cations by either acids or chelating reagent such as EDTA improves the cleaning of membranes fouled by organic foulants.

Surfactants

Surfactants are compounds that have both hydrophilic and hydrophobic structures. They can form micelles with fat, oil, and proteins in water and help to clean the membranes fouled by these materials. One interesting but less clear aspect is how surfactants affect membrane fouling dominated by NOM (natural organic matter). As the surfactant is nonionic, the interaction between the membrane and the surfactant is dominated by hydrophilic and hydrophobic reaction. Since the membrane is hydrophobic, hydrophilic tail of the surfactant is preferably adhered to the membrane surface and hydrophilic head is orientated toward aquatic phase. Soaking in surfactant has been used as a method for surface modification to improve hydrophilicity or wettability of certain membranes.

Operating Parameters Affecting Cleaning Efficiency During Chemical Cleaning

Because membrane cleaning is essentially conducted through chemical reactions between cleaning chemicals and fouling materials, factors that affect the mass transfer and chemical reactions such as concentration, temperature, length of cleaning period, and hydrodynamic conditions affect the efficiency of cleaning.

When selecting cleaning conditions, ensure the compatibility of cleaning chemicals with membrane media and filters and systems. Chemical

compatibility of membrane and filter components limits the type and the maximum allowable concentration of a chemical to be used during cleaning.

Concentration of cleaning chemicals can affect both the equilibrium and the rate of reaction. The concentration profile of cleaning chemicals within the fouling layer is a function of the concentration of cleaning chemicals in the bulk liquid phase. Therefore, the concentration of cleaning chemicals not only need to maintain the reasonable reaction rate (kinetics need) but also need to overcome mass transfer barrier imposed by the fouling layer. In practice, the concentrations of cleaning chemicals are usually high enough to satisfy the kinetic need. It is the mass transfer that sets the lower boundary for the concentration of cleaning chemicals.

Temperature can affect membrane cleaning by:

- Changing the equilibrium of a chemical reaction
- Changing the reaction kinetics
- Changing the solubility of fouling materials and/or reaction products during the cleaning

From mass transfer point of view, dynamic cleaning involving circulating cleaning solutions through the system can be more effective than simply static cleaning such as soaking.

RO Membrane Element Cleaning and Flushing Procedures

The RO membrane elements can be cleaned in place in the pressure tubes by recirculating the cleaning solution across the high-pressure side of the membrane at low pressure and high flow. A cleaning unit is needed to do this. RO cleaning procedures may vary depending on the situation. The time required to clean a stage can range from 4 to 8 h.

A general procedure for cleaning the RO membrane elements is:

- Perform a low-pressure flush at 60 psi (4 bar) by pumping clean water from the cleaning tank through the pressure tubes to drain for several minutes. Flush water should be clean water of

RO permeate or DI (deionized) quality water and be free of hardness, transition metals, and chlorine.

- Mix a fresh batch of the selected cleaning solution in the cleaning tank. The dilution water should be clean water of RO permeate or DI quality and free of hardness, transition metals, and chlorine.
- Circulate the cleaning solution through the pressure tubes for about 1 h or as required. At the start, send the displaced water to drain so you do not dilute the cleaning chemical and then divert up to 20 % of the most highly fouled cleaning solution to drain before returning the cleaning solution back to the RO cleaning tank. For the first 5 min, slowly throttle the flow rate to one third of the maximum design flow rate. This is to minimize the potential plugging of the feed path with a large amount of dislodged foulant. For the second 5 min, increase the flow rate to two third of the maximum design flow rate and then increase the flow to two third of the maximum design flow.
- An optional soak and recirculation sequence can be used, if necessary. The soak time can be from 1 to 8 h depending on the manufacturer's recommendations but not to exceed maximum pH and temperature limits for specific elements.
- Upon completion of the chemical cleaning steps, a low-pressure cleaning rinse with clean water (RO permeate or DI quality and free of hardness, transition metals, and chlorine) is required to remove all traces of chemical from the cleaning skid and the RO skid. Drain and flush the cleaning tank; then completely refill the cleaning tank with clean water for the cleaning rinse. Rinse the pressure tubes by pumping all of the rinse water from the cleaning tank through the pressure tubes to drain.
- Once the RO system is fully rinsed of cleaning chemical with clean water from the cleaning tank, a final low-pressure cleanup flush can be performed with pretreated feed. The permeate line should be open to drain. Feed pressure should be less than 60 psi (4 bar). This final flush continues till the flush water is clean and is free of any foam or residues. This flush goes

for 15–60 min. A conductivity meter can be used to test for removal of cleaning chemicals, such that the flush water to drain is within 10–20 % of the feed conductivity. A pH meter can also be used to compare the flush water to drain to the feed pH.

- Once all the stages of a train are cleaned, and the chemicals flushed out, the RO plant can be restarted and placed into a service rinse. The RO permeate should be diverted to drain until it meets the required quality of the process. It normally takes few hours to few days for the RO permeate quality to stabilize, especially after high pH cleanings.

Conclusion

As the water treatment industry grows at a remarkable pace, the ability to treat aggressive surface and waste waters that are notorious for having high organics, colloids, and biological fouling potential continues to be challenging.

Using a generic or commercial alkaline cleaning chemical significantly affects OPEX, while the payback primarily depends on the chemicals used. Cleaning to reduce a facility OPEX depends on water temperature, energy costs, and chemical costs. Establish a cleaning strategy that is most effective and well tested; analyze the foulants followed by an autopsy protocol. Selection of an appropriate pretreatment with good operation and maintenance practices will lead to cost-effective cleaning regime. The cleaning efficiency depends on the type of cleaning agent and its concentration. The net effect is that the efficiency increases with increasing chemical concentration. Operating parameters such as cross-flow velocity, turbulence in the vicinity of membrane surface, temperature, pH, and duration of cleaning affect the cleaning process. Analyze the right cleaning strategy on a case-by-case basis. It is recommended that the MSDS (Material Safety Data Sheet) of the cleaning chemicals be procured from the chemical supplier and knowledge be applied in the handling and storage of the chemicals.

Cross-References

- ▶ [Cleaning Cycle of Fouled Membranes](#)
- ▶ [Cleaning Effectiveness](#)
- ▶ [Cleaning Efficiency](#)
- ▶ [Fouling Index](#)
- ▶ [Fouling in Membranes](#)
- ▶ [Fouling Release](#)
- ▶ [Fouling Release Membranes](#)
- ▶ [Natural Organic Matter, Removal and Fouling of](#)

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Chemical Industry and Membrane Operations

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Chemical industry is a complex of processes, involved in the manufacture of chemicals and their derivatives. Generally, a production cycle comprises the conversion of raw materials and the product recovery and purification. Separation processes are among the most energy-intensive stages. Membrane technology is widely accepted and well established in the chemical industry, allowing to decrease equipment size, raw

materials, and energy utilization, as well as waste generation, in the process intensification logic (Stankiewicz and Moulijn 2000). Membrane processes have several advantages than conventional separation techniques (e.g., distillation, extraction, absorption, and adsorption), including modularity and compactness, operational flexibility, no need for energy-intensive phase changes, or potentially expensive adsorbents and/or difficult-to-handle solvents.

The separation of hydrogen from nitrogen in ammonia plants was the first large commercial application of membrane-based gas separation (Bernardo et al. 2009). Compact and modular membrane modules, mainly in the form of hollow fibers, are widely used for nitrogen production to inert fuel tanks, also aboard aircrafts, and for blanketing chemical, methanol, and liquefied gas shipments to enrich oxygen for medical uses, for hydrogen recovery and purification, for air and gas dehydration, and for ratio adjustment of gas mixtures.

Membranes represent a valid alternative to chemical treatment in the wastewater treatment, producing a cleaner and more reliable effluent for discharge or recycle, reducing, at the same time, chemical, analytical, and labor costs. Membrane technology has a significant role in the production of different grades of process water and in a recycle/reuse logic. Depending on the nature and variability of the feed supply, ultrafiltration or microfiltration membranes can effectively perform the pretreatment for reverse osmosis, removing bacteria and solid particles (Lefebvre and Moletta 2006). Membrane bioreactors, by combining the traditional biological degradation with a solid–liquid separation by means of low-pressure membrane filtration (ultrafiltration or microfiltration), are appropriate solutions in the industrial wastewater treatment to reduce plant footprint and operating costs (Marrot et al. 2004).

Filtration membranes are variously used for concentration and/or recovery purposes in different industrial cycles: in the production of pigments, surfactants, electronics, textiles, pulp, and paper, in the industrial laundering, and in the chemical and mineral processing. Acid- and

base-stable membranes, based on ceramic materials, are suited for the concentration and demineralization of dyes in acids; the decolorization, clarification, or demineralization of spent acid and caustic solutions for recycle; and the concentration, desalination, and softening of in-process and waste streams and for COD and BOD reduction in waste streams such as pulp and paper waste effluents.

Pervaporation allows organic dewatering, especially from ethanol and isopropanol (Van der Bruggen 2009). The development of solvent-stable membranes has permitted the progress of organic solvent nanofiltration which is applied for nonthermal solvent recovery; in situ recycling of organic solvents; purification, and concentration of intermediates; product upgrading; and continuous recovery of homogeneous catalysts (White 2006). Moreover, significant progresses have been done in the recent years in developing other unit operations such as membrane reactors (Shirasaki et al. 2009) and membrane contactors (Klaassen et al. 2005), covering all the chemical engineering unit operations. Membrane contactors, accepted into the beverage industry for carbonation, deaeration, and nitrogenation, are effectively used in degassing applications and corrosion control.

The range of application of the membrane technology could be extended with the availability of new membrane materials able to withstand more demanding process conditions of temperature, pressure, and aggressive conditions. Other interesting options are related to hybrid systems in which membrane technology is combined with another separation process, improving overall process efficiency and offering the opportunity of developing, reengineering, or retrofitting chemical processes (Koltuniewicz 2010).

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Chemical Looping

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Among different strategies for CO₂ capture, a new emergent technology is focusing the attention: chemical-looping combustion (CLC). This novel concept could reduce up to 50 % of the costs of CO₂ capture in regard to current technologies. For that reason, the IPCC remarked CLC as one of the cheapest technologies for CO₂ capture. It was in 1987 when Ishida et al. introduced by the first time the term chemical-looping combustion for power generation and later as a powerful technology for CO₂ capture (Ishida and Jin 1994; Ishida et al. 1987). The technology is referred to as a

cycling system where a solid with high oxygen capacity called oxygen carrier transfers the oxygen needed to convert the fuel. By this way, CO_2 produced by the combustion of the fuel is not diluted in the N_2 (from the air) because direct contact between fuel and air is avoided. Hence a CO_2 -rich stream is produced at the exit point of the reactor. It implies lower energy requirements for CO_2 capture than other strategies where CO_2 and N_2 are mixed. The main drawback of this technology is the lack of maturity, and for that reason the interest in the system has increased during the last years as can be discussed in the recent review by Adánez et al. (2012). More than 700 different oxygen carriers have been already tested, and the performance of the concept has been tested in different CLC units in the size range 0.3–120 kW_{th}.

Chemical looping systems have not been exclusively focused on fuel combustion for power generation but also for fuel reforming (mainly methane) for syngas production. This concept is called chemical-looping reforming (CLR). The CLR occurs if at the fuel reactor the CH_4 is fed with steam and with a lower amount of oxygen (compared to the CLC) contained in the oxygen carriers. In this way, the fuel conversion gives a reformed syngas with high H_2 concentration. The system behaves like an autothermal reformer, and the heat for the endothermic reaction is directly supplied by burning part of the methane. It has been operated for short times in lab-scale systems at moderate pressures (Rydén and Lyngfelt 2006; Rydén et al. 2008a, b). In total around 100 h operation of CLR have been demonstrated worldwide (Adanez et al. 2012). The main research in literature has been focused on oxygen carrier studies for reforming of natural gas. The typical reactor scheme of CLR is similar to the well-known CLC but differs in the desired product, which in CLC is heat and in CLR is syngas. Recently, Gallucci et al. proposed the application of a chemical-looping reforming where the fuel reactor is replaced by a membrane-assisted fluidized bed reactor. This new concept named membrane-assisted chemical-looping reforming (MA-CLR) gives many advantages over the previous concepts especially because a

much higher hydrogen recovery can be obtained at lower temperatures.

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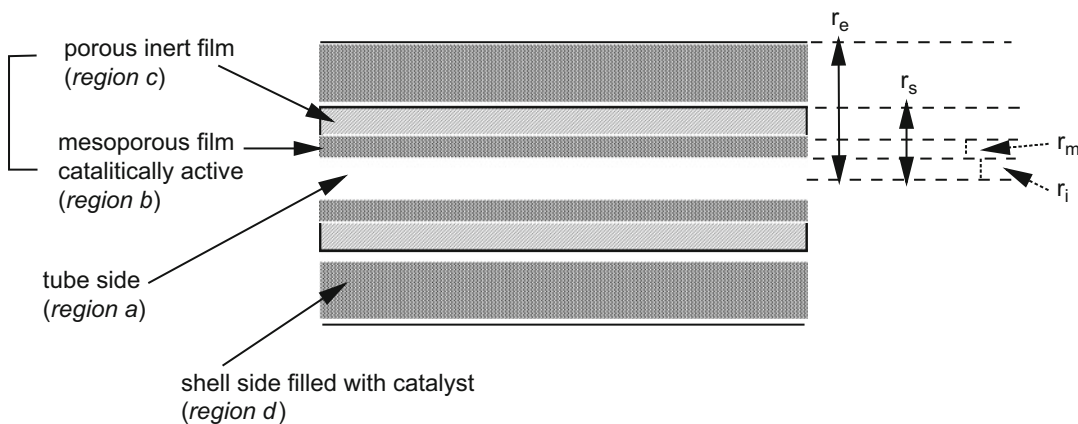
Chemical Membrane Reactors

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Chemical membrane reactors are membrane reactors using chemical catalysts, mainly of inorganic origin.

Both dense and porous membranes are used in membrane reactors. Dense membranes are made of polymers, metals and their alloys, and solid oxides. Dense metal membranes mostly consist of Pd, Pt, Ru, Rh, Ag, and their alloys. Pd membranes and its alloys are used for dehydrogenation reaction. They have high selectivity toward hydrogen, while Ag membranes are selective toward oxygen.



Chemical Membrane Reactors, Fig. 1 Packed bed membrane reactor with the membrane formed of a mesoporous film catalytically active and a porous inert support layer

Solid oxides (ZrO_2 , BiO_3 , Y_2O_3) and solutions of mixed solid oxides (such as perovskite-type oxides) have been used as dense membranes selective for oxygen or hydrogen. They are used in catalytic membrane reactors for partial and total oxidation reactions.

Mesoporous membranes made of alumina, titania, and zirconia are also used to prepare membrane reactors. Microporous membranes made of zeolites have been also prepared.

As a general example of modeling of chemical membrane reactors, here is reported the case of a packed bed membrane reactor with the membrane formed of a mesoporous film catalytically active and a porous support layer inert (Fig. 1). The tube and shell sides are occupied by packed bed catalysts.

The reaction occurs in gas phase. The gas transport through the mesoporous membrane layer takes place by Knudsen diffusion. Surface flow and diffusion through the porous region are considered to be negligible. The reaction could take place inside the catalytically active membrane and/or in the packed beds placed in the tube- and/or shell-side compartments. Based on these assumptions, the model equations in cylindrical coordinates and the corresponding boundary conditions for each region showed in the Fig. 1 are described as follows:

In the tube side (*region a*):

$$V_f \frac{\partial C_i^a}{\partial z} = D_i^a \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i^a}{\partial r} \right) - \rho_b \alpha_i v^a \quad (1)$$

with $0 \leq r \leq r_a$ and $0 \leq z \leq L$.

V_f is the superficial fluid velocity (m s^{-1}); C_i^a is the concentration of species i in region 1; D_i^a is the effective radial diffusivity through the packed bed in the tube; ρ_b is the reactor bed density; α_i is the stoichiometric coefficient; and v^a is the apparent reaction rate ($\text{mol kg}^{-1} \text{s}^{-1}$).

In the reactive membrane (*region b*):

$$D_i^b \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i^b}{\partial r} \right) = \rho_m \alpha_i v^b \quad (2)$$

$$r_i \leq r \leq r_m$$

ρ_m is the membrane density; D_i^b is the membrane diffusivity; and v^b is the observed reaction rate.

In the macroporous support (*region c*):

$$D_i^c \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i^c}{\partial r} \right) = 0 \quad (3)$$

$$r_m \leq r \leq r_s$$

In the shell region (*region d*):

$$U_d \frac{\partial C_i^d}{\partial z} = D_i^d \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i^d}{\partial r} \right) - \rho_b \alpha_i v^d \quad (4)$$

$$r_s \leq r \leq r_e$$

$$0 \leq z \leq L$$

Catalytic Membrane Reactors with Nonselective Membrane (CNMR)

In these types of membrane reactors, the membrane may act as a contactor device (catalytic) or may serve to distribute reactants in an uniform way (inert). In modeling such reactors, Knudsen diffusion as well as molecular diffusion and convective transport may occur. The dusty gas model of transport is typically utilized. Membrane reactors using mesoporous membranes and operating under a transmembrane pressure gradient may also use this model. For such reactors, an isothermal model that consists of mass balance equations in every membrane compartment can be used. For example, for compartments where reaction occurs, the mass balance is

$$\nabla J_i = V_{r_i} \quad (5)$$

while in nonreactive regions

$$\nabla J_i = 0 \quad (6)$$

where J_i is the flux of species i and V_{r_i} is the corresponding reaction rate. According to the dusty gas model, J_i is described as:

$$\sum_{j=1, j \neq i}^n \frac{X_i J_i - X_j J_j}{PD_{ij}} - \frac{J_i}{PD_{ik}} = \frac{1}{RT} \nabla x_i + \frac{J_i}{PRT} \left(\frac{B_0 P}{\mu D_{ik}} + 1 \right) \nabla P \quad (i = 1 \dots n) \quad (7)$$

where D_{ij} is the effective binary diffusion coefficient of components i and j (already includes the

porosity and the tortuosity of the membrane), D_{ik} is the corresponding effective Knudsen diffusion coefficient, and x is the molar fraction. B_0 corresponds to the permeability coefficient for convective flow in m^2 , and μ is the viscosity in $\text{N}\cdot\text{s}/\text{m}^2$. D_{ij} , D_{ik} , and B_0 are empirical parameters, which depend on the structure of the porous membrane.

Chemical Pretreatment

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Definitions

The term *chemical pretreatment* refers to the use of coagulant chemicals to form flocculant (floc) particles in a water-based feed stream to enhance contaminant removal.

Objectives

The purpose of chemical pretreatment is to entrap particulates and to some extent dissolved contaminants, for subsequent removal by gravity settlement or flotation, or by removal in a physical filtration step (see *granular media pretreatment* and *physical pretreatment*).

Process Principles and Mechanisms

Water treatment relies on settlement to remove large particles, followed by filtration to remove finer ones. A wide variety of particulate and dissolved contaminants can be found in water and wastewater sources (Parsons and Jefferson, 2005). Larger particles are held in suspension in a flowing stream and settle rapidly if the feed is stored. As particle size becomes finer, settling velocities reduce sharply and below a size of 10 μm , rates become so low that it is not practical

to remove these contaminants by settlement processes alone, as illustrated in Table 1.

In a typical water source, fine particles are held in suspension in a stable dispersed state. There are forces of gravity attraction between particles, but for small particles, the forces are not sufficient to lead to natural agglomeration, which would aid their removal by settlement. Indeed, forces of electrostatic repulsion tend to prevent particles coming together, particularly for submicron sizes, and the random forces of Brownian motion contribute to maintaining colloids and macromolecules in suspension.

Colloids can give rise to turbidity and affect other aesthetic water quality parameters such as color and so need to be removed in the water

treatment process. If derived from organic matter such as algae, they may cause fouling in downstream processes such as RO, or could be responsible for toxic residuals in treated water.

Coagulation is the process used to destabilize the dispersed suspended matter as illustrated in Fig. 1. The colloids tend to have a negative charge at the surface which generates a significant repulsion between particles. The coagulant neutralizes the surface charge and overcomes the repulsive forces. In the figure, trivalent Al^{3+} ions are used to fulfil this role.

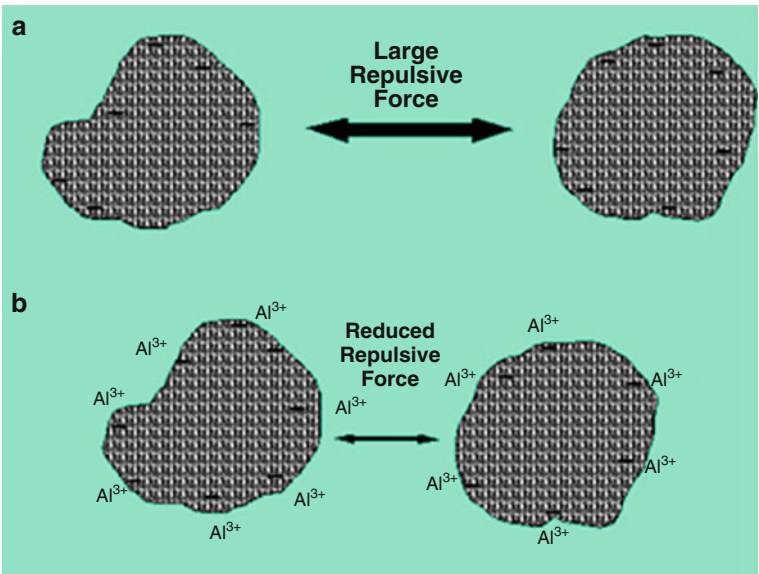
Hydrophilic molecules and ionic species have strong bonds of hydration to water molecules which assist their stable dissolution in water. In contrast, hydrophobic molecules do not bond to water and are easy to separate from a bulk water medium. However, naturally occurring dissolved organic molecules and colloids are often amphiphilic in nature having a portion of the molecule which is hydrophilic (water loving) and a portion which is oleophilic (oil loving). The oleophilic portion is likely to also be hydrophobic (water hating), giving rise to the synonymous term amphipathic.

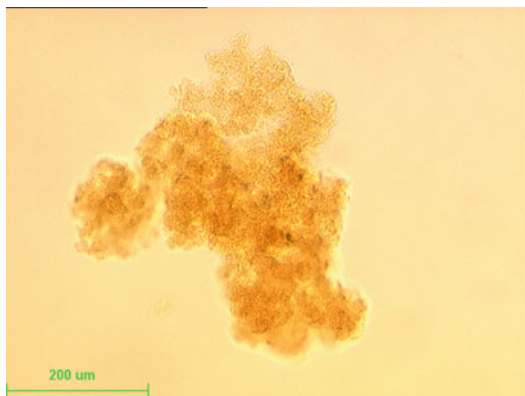
Common contaminants in surface water include humic and fulvic acids which are responsible for color and can give rise to disinfection

Chemical Pretreatment, Table 1 Settling velocities for common particles and colloids

Particle diameter mm	Type	Settling velocity
10	Pebble	0.73 m/s
1	Coarse sand	0.23 m/s
0.1	Fine sand	0.6 m/min
0.01 (10 μ m)	Silt	8.6 m/day
0.0001 (0.1 μ m)	Large colloids	0.3 m/year
0.000001 (1 nm)	Small colloids	3 m/million year

Chemical Pretreatment, Fig. 1 Colloid destabilization





Chemical Pretreatment, Fig. 2 Floc particle

by-product residuals after chlorination. These macromolecules are examples of colloids with strong amphiphilic character. Coagulants assist in the removal of these colloids by displacing hydration water from the hydrophilic portion of the molecule and associating with the hydrophobic portion through charge attraction. The Al^{3+} sites then attract hydration water and the partly neutralized particle agglomerates with other coagulated particles to create the rapid buildup of a floc particle as shown in Fig. 2.

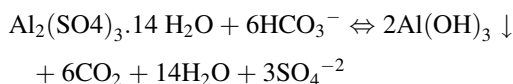
The initial dispersion phase takes between 10 and 120 s. Once the coagulation process has been initiated, the process of flocculation can then proceed, i.e., the agglomeration of the destabilized particles. The growth phase can take up to 40 min, though in commercial processes, it is normal to use considerably less time than this. The initial seed for the floc to form is normally a small particle or colloid, but as it grows, dissolved organics become associated with the floc due to their charge or surface character and can therefore be removed from the bulk liquid phase. Coagulation can therefore be used to reduce total suspended solids and turbidity, and to some extent dissolved organics, thereby providing a significant impact for the improvement of water quality.

Coagulant Chemical Categories

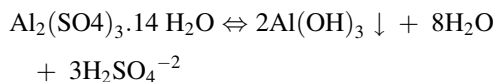
Dosing chemicals fall into three categories:

- Inorganic coagulants
- Inorganic polymeric coagulants
- Organic polymeric coagulants

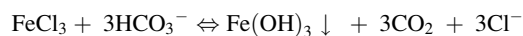
The most common inorganic coagulants used in water treatment are Al^{3+} salts added as aluminum chloride or aluminum sulfate (alum) and Fe^{3+} salts added as ferric chloride or ferric sulphate (Bache and Gregory, 2007). The coagulation reaction of alum is shown below:



The optimum pH for the hydrolysis reaction shown is 5.5–6.5. However, note that the reaction conditions are only satisfied for feed water with a significant level of bicarbonate alkalinity. According to the equation above, 1 mol of alum consumes 6 mol of bicarbonate, so in a soft, low alkalinity water, there may not be sufficient naturally occurring calcium bicarbonate to support the required reaction. In this case, the reaction generates sulfuric acid, causing the pH to drop sharply, as shown in the following equation. Note that lime addition would be required to neutralize:



Ferric chloride consumes half the molar concentration of bicarbonate in its hydrolysis reaction since there is only one ion of Fe^{3+} for each ferric chloride molecule, whereas the sulfate in alum is divalent. The hydrolysis equation is:



The optimum pH for Fe^{3+} is 4.5–5.5, but there is a wider range of pH that can be used in different circumstances of 4–9. Thus, Fe^{3+} is less pH sensitive than Al^{3+} and normally provides better turbidity, color, and natural organic matter (NOM) removal at a given molar concentration. As with Al^{3+} , acidity will be created if the bicarbonate concentration is insufficient, requiring lime addition.

Due to the higher density of floc particles with Fe^{3+} , the sludge has better settleability and is often preferred for clarification applications. Fe^{3+} produces a higher sludge mass. Al^{3+} can struggle in cold water conditions, but is often preferred for dissolved air flotation, since this process relies on the low density of the floc particle. In some countries Fe^{3+} is preferred to Al^{3+} for health reasons.

The basic coagulation chemistry of both inorganic and organic polymeric coagulants is similar to the straightforward inorganic coagulants, but the pH tolerance may be wider and the effectiveness of the coagulation and subsequent flocculation reactions may be improved. The most common coagulant in the second category is polymeric aluminum chloride (PACl), which is used to overcome problems associated with Al. PACl has better binding with clays, etc. due to higher charge density. In general water treatment, poly-aluminum coagulant hybrids can be used, but these are not often encountered in UF pretreatment, though aluminum chlorohydrate (ACH) is found to be effective. Coagulants with a higher charge density can be more effective at neutralizing the negative charge of colloids and will tend to initiate agglomeration more rapidly, growing stronger floc particles.

The third category of coagulant is the organic polymeric category. The most common example in this group is the cationic polymeric coagulant PDADMAC which has a high charge density giving good removal of clays and organics. It can be typically used at 10 % of the inorganic coagulant concentration and has low sludge yield. Some cationics can bind to membrane surfaces, so UF users are very cautious and the often chemically related category of floc aid is also used with great care due to the risk of attachment. Fortunately, floc aids are not normally needed in membrane pretreatment.

In summary, both Fe and Al compounds are widely used in chemical pretreatment, but Fe is more often selected for use in membrane pretreatment, utilizing low dosing concentrations. PACl is sometimes successfully employed, but high-performance organic coagulants are less often used due to cost and concerns about fouling. The low coagulant concentrations provide a key

advantage in reducing sludge disposal costs, and this is likely to become an even more important factor in the future, outweighing chemical purchase cost considerations in some circumstances.

Coagulation Conditions

Establishing the correct conditions for coagulation first requires a selection of the correct coagulant from the options described in the previous section. The appropriate coagulant concentration and pH will then need to be determined, as well as the correct physical conditions. These requirements may vary depending on the process selected for the formation and removal of the floc. Choosing the right coagulant often requires a review of comparable applications in terms of feed water type and temperature, with similar process requirements. If there is no direct comparison, several alternatives might need to be explored.

The next step is to determine the best conditions for the coagulant chosen. This is normally carried out by conducting jar tests. In these tests, a number of beakers are set out with the feed and coagulant at different concentrations and pH conditions. A typical jar test set up is shown in Fig. 3.

As well as varying coagulant concentration, another series of tests may be carried out at a promising concentration with a variation of the pH from say 5.0–7.5 in increments of 0.5 of a pH unit between jars. The jars are mixed in a consistent way with the addition of the coagulant and the time noted for floc formation. A typical procedure would use 1 min of rapid mixing at 100–150 rpm to ensure quick dispersion of the coagulant throughout the mixture, followed by a period of 14 min at a slow mixing speed of say 25–30 rpm. The emergence of floc is noted, and the turbidity of the supernatant is measured once stirring has stopped. It is also instructive to observe floc settleability. A plot of residual turbidity against pH as shown in Fig. 4 will indicate the optimum coagulation condition, which in the case of the graph above is 6.3

Chemical Pretreatment,

Fig. 3 Jar test showing different Al^{3+} concentrations with a 15 min contact time

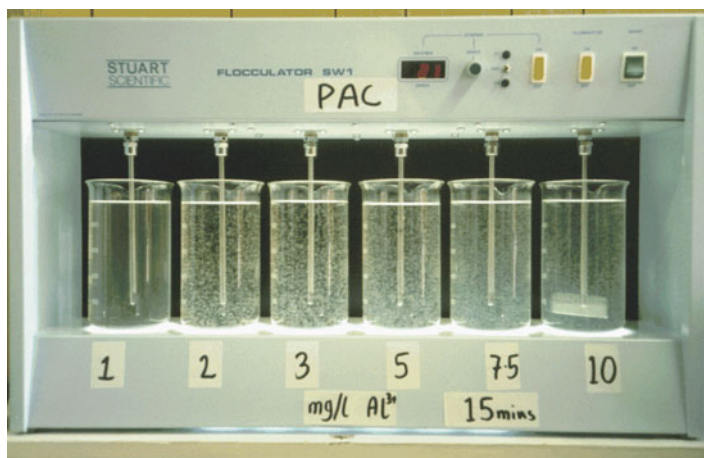
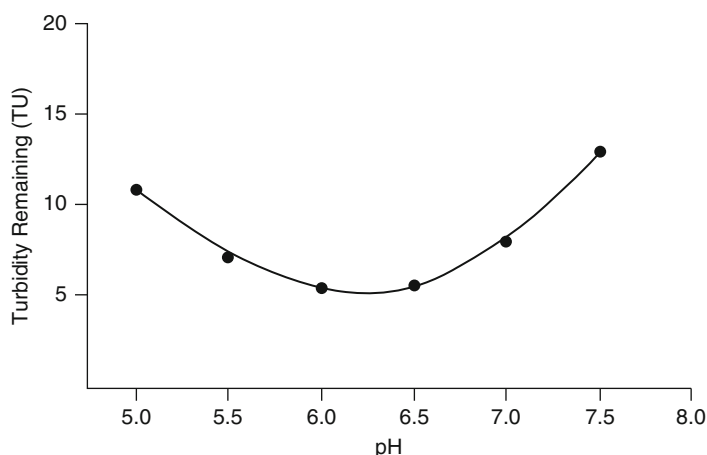
**Chemical Pretreatment,**

Fig. 4 Residual turbidity versus pH

**Process and Implementation**

In water and wastewater treatment, coagulation is often required to improve the removal performance of conventional processes such as sand filters. For a conventional process flow scheme, the coagulation step is normally conducted prior to filtration using a clarifier or dissolved air flotation (DAF) unit. Membrane processes are less reliant on coagulation, but they are still used quite frequently. Wastewater reuse applications always use coagulant and it is used in over half of surface water capacity and also quite frequently in seawater treatment. However, the use of coagulants in groundwater treatment is unusual.

The key issue for coagulant addition is to ensure a rapid dispersion of the dosed chemical after the injection point so that it is well dispersed through the bulk liquid, followed by an opportunity for the floc to grow in relatively low shear conditions. Rapid dispersion requires a good mixing stage which can be achieved by a dosing injection point immediately prior to a pump or strainer, thereby using the pump impeller or strainer media to achieve the mixing. Alternatively an in-line mixer can be used in the pipe just after the injection point, or if in a tank, a baffled flowpath is created. It is important that process shear is applied immediately after injection, i.e., within the first few seconds. Once the

floc has formed and starts to grow, high shear operations may break up the floc, and it could be difficult to get the floc to regrow. This can cause high turbidity and fouling of downstream unit operations.

In general, coagulation in membrane pretreatment flow schemes may be considered for the following reasons:

- Improve general feed quality to increase UF/MF flux
- Ameliorate feed quality excursions such as turbidity spikes and, in the case of seawater pretreatment, algal bloom, and red tide events
- Reduce dissolved organic concentration to lessen biofouling

Operational Issues

It is important for a coagulant to produce a floc which will be effectively removed in downstream process operation. If the removal is to be achieved by settlement in a clarifier, the floc needs to be large, dense, and fairly robust. For filtration through a granular media filter, the floc needs to be large and robust. Sometimes, a polymeric coagulant or floc aid could be used as a floc strengthener or enlarger to assist growth of the floc to improve removal by settlement or filtration, and make it less likely that the floc will be broken up through process shear. If it is to be removed in a dissolved air flotation unit, the floc needs to be low in density. If the floc is formed by direct in-line injection just prior to a membrane filtration stage, it is likely that a microfloc would be sufficient.

Although clarifiers or DAF are sometimes used upstream of the membrane in some pretreatment applications, a significant proportion of membrane systems use in-line dosing at low coagulant dose with a minimal contact time at 20–30 s. This has provided the opportunity for membrane systems to cut coagulant doses radically from levels of several ppm used for clarification or DAF to 1 ppm or less (as Fe^{3+}) for in-line dosing.

The main concern in the use of coagulants with membrane pretreatment processes is the

danger of coagulant fouling, potentially both of the UF or MF membrane and/or of any downstream RO. This may occur due to overdosing or floc disruption from shear, either as a result of pumping or excessive transmembrane pressure (TMP). In seawater applications, the current trend is to eliminate in-line dosing during good feed quality periods and to use a low and variable dose during periods of poor or variable quality. Different membranes respond differently to coagulants, and so selection of the coagulant procedure is often carried out through pilot trials or comparison with other operations using similar feeds.

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Chemical Vapor Deposition

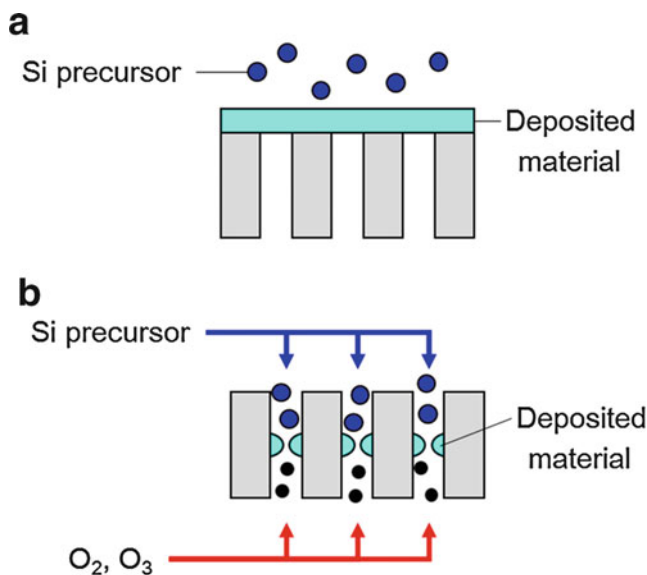
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Chemical vapor deposition (CVD) is a method for depositing thin films of various materials (Smith 1995). CVD process involves a series of gas phase and surface reactions of volatile precursors, which are induced by, for example, heat, light, and/or plasma-discharge. CVD has been used extensively in a number of industries such as semiconductor, electronics, and optics industries.

CVD techniques have also been utilized in the fabrication of inorganic molecular sieve membranes. Among the types of CVD technique, thermal CVD has been most extensively studied since Gavalas and coworkers first reported successful synthesis of the hydrogen-selective silica membranes in 1989 (Gavalas et al. 1989). There are

Chemical Vapor Deposition,

Fig. 1 Schematic diagram of (a) one-sided and (b) counter-diffusion CVD processes



two types of reaction geometries available for thermal CVD, as shown in Fig. 1: one-sided CVD and counter-diffusion CVD (Nomura et al. 1997; Nakao et al. 2000). For the case of the one-sided CVD, all of the reactants are fed to the same side of the porous substrate, and then, the film-forming reactions occur at the surface of the substrate. On the other hand, for the case of the counter-diffusion CVD, the reactants are fed to the opposite side of the substrate. The reactants diffuse into the porous substrate and the reactions take place at the location where the reactants contact each other. Therefore, the deposition occurs inside the pores and the pore size will be decreased. The deposition continues until the pore size becomes small enough to reduce diffusion of the reactants. As a result, uniform pore size can be obtained by using the counter-diffusion CVD.

The hydrogen-selective silica membranes reported by Gavallas et al. were prepared by depositing a dense silica layer on the top of Vycor glass membranes by the oxidation of SH₄ at 450 °C (Gavallas et al. 1989). The obtained membranes were reported to have high H₂/N₂ selectivities as high as 3,000 but low H₂ permeances of 2.1×10^{-8} mol/(m² s Pa) at 450 °C. Until then, a great deal of progress has been made by several research groups. For

example, Gu and Oyama prepared a silica membrane on the substrate with a graded γ -alumina intermediate layer by the thermal decomposition of tetraethoxysilane (TEOS) at 600 °C and reported H₂ permeance of 5.0×10^{-7} mol/(m² s Pa) at 600 °C, with H₂/CH₄ selectivity of 5,900 (Gu and Oyama 2007). Ohta et al. prepared silica membranes on the γ -alumina intermediate layer by using oxidation of tetramethoxysilane (TMOS), phenyltrimethoxysilane (PTMS), or dimethoxydiphenylsilane (DMDPS) at 600 °C and reported that larger pores were formed when the number of phenyl groups on the precursor was increased (Ohta et al. 2008). The DMDPS-derived membrane showed a high H₂ permeance of the order of 10^{-6} mol/(m² s Pa) at 300 °C, with H₂/SF₆ selectivity of 6,800.

Plasma-enhanced CVD (PECVD) is another type of CVD technique utilized for the membrane fabrication. PECVD offers a low processing temperature compared with thermal CVD due to the high reactivity of plasma. Several research groups reported the PECVD-derived membranes prepared at room temperature by using several kinds of precursors such as hexamethyldisiloxane (HMDSO) (Roualdes et al. 2002; Tsuru et al. 2011; Nagasawa et al. 2013), hexamethyldisilazane (HMDS)

(Kafrouni et al. 2009), or bis(dimethylamino) dimethylsilane (BDMADMS) (Kafrouni et al. 2010). Typical PECVD-derived membranes showed moderate selectivity (e.g., He/N₂ selectivity of <10 at 25 °C and ~30 at 150 °C) with He permeance of the order of 10⁻⁸–10⁻⁷ mol/(m² s Pa), probably because the PECVD-derived layer remains to have high content of organofunctional groups which make the structure more loose (Roualdes et al. 2002; Tsuru et al. 2011; Nagasawa et al. 2013; Kafrouni et al. 2009, 2010). Selectivity of PECVD-derived membranes can be improved by 2-step PECVD sequence, which involves HMDSO/Ar-PECVD followed by HMDSO/O₂-PECVD (Tsuru et al. 2011; Nagasawa et al. 2013). Moreover, the membrane prepared via 2-step PECVD showed a good thermal stability, although the membrane was fabricated at room temperature. The 2-step PECVD-derived membrane showed high He and H₂ permeances of 5.2 × 10⁻⁷ and 2.4 × 10⁻⁷ mol/(m² s Pa) at 400 °C, respectively, with He/N₂ and H₂/N₂ permeance ratios of 4,200 and 1,900, respectively (Tsuru et al. 2011; Nagasawa et al. 2013).

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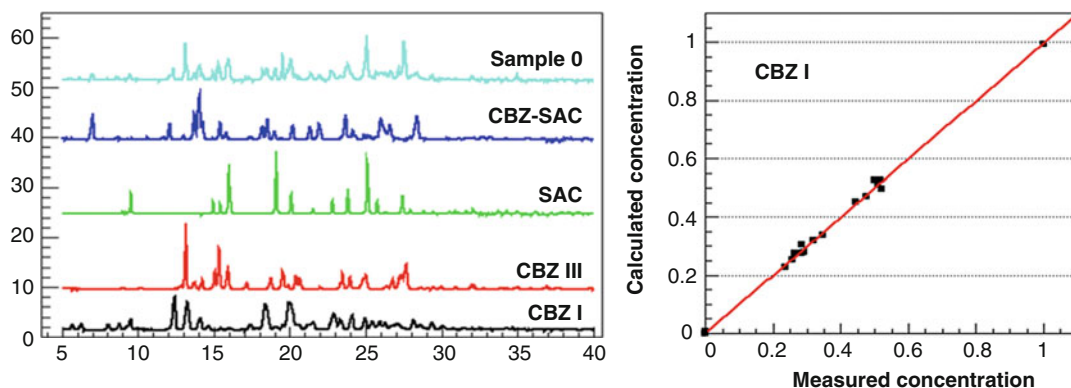
Chemometrics

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Chemometrics can be defined as “information aspects of chemistry”, where statistical and mathematical methods are used to produce “good data” and to extract relevant information from measured data (Wold and Sjostrom 1998). The first aim can be achieved by using design of experiments (DoE) to provide a small number of information-rich experiments. Multivariate data analysis and advanced data visualization can be employed for the second purpose. In fact, multivariate projection methods can be used to simplify complex data and thus make the visualization easier. Furthermore they can be used for classification of samples and to predict outcomes.

Theory of DoE and literature with references covering the field of experimental design and optimization can be found in Box et al. 1978; Gabrielsson et al. 2002; Lundstedt et al. 1998; Mandenius and Brundin 2008. Instrumentation developed in the field of process analytical chemistry (PAC) supplies data about the state of a process (Callis et al. 1987). Combination of PAC instrumentation and multivariate analysis provides tools for effective process monitoring



Chemometrics, Fig. 1 X-ray diffraction profiles and calibration plot of a PLS model for quaternary carbamazepine-saccharin mixtures

and control enabling detection of multivariate relationships between different variables such as raw materials, process conditions, and end products.

DoE represents a special case of predictive modeling. The objective of predictive modeling is to determine the relationship between several x-variables (often called independent or explanatory variables) and one or more y-variables (dependent or response variables). This objective can be achieved by means of a regression model, where the observed result, i.e., response (y), is described as a function of the x-variables. Models can be seen as tools to describe reality. Empirical models based on the experimental data can be estimated and used for interpretation and prediction. All models are more or less erroneous, since there are always noise and other irrelevant features in the data. Experimental error is produced by both known and unknown disturbing factors that may confound important effects wholly or partially. This can be reduced and sometimes almost eliminated by using DoE and statistical analysis.

Multivariate data analysis has proven to be a powerful tool when combined with advanced characterization techniques. Apart from regression models, it also uses latent variable methods, such as principal component analysis (PCA) and partial least squares (PLS), for classification and prediction purposes. Measured variables, which describe partially or fully the same property of a

system, provide similar information content. Collinear variables can be combined and described by fewer, so-called factors or latent variables, which describe the underlying structure in the data. In modeling, the prime aim is to separate information from noise and find the crucial patterns in the data. Following the introduction of computers and computerized measurement techniques, latent variable methodology has penetrated nearly all areas where complex systems are measured and modeled, and it is especially powerful when huge amounts of data are produced and systematic approaches are needed to reveal the information in the data.

In the framework of membrane technology, chemometrics can be used for process optimization, which includes quality control of components, and for characterizing the products of the process. For example, in the process of membrane crystallization, chemometrics allows to find the best setting of parameters ruling the process (solvent flux, precipitant and solute concentrations, temperature, geometry, amount of solution), to control the quality of the membranes and plates used, and to characterize the crystals produced. Regression models allow to predict crystallization products given a set of (unexplored) parameter setting. As an example, the X-ray diffraction profiles measured for mixtures formed by polymorph III of carbamazepine, saccharin, and cocrystal carbamazepine-saccharin produced by

membrane crystallization have been processed by PLS, which are able to supply precise quantitative predictions on their concentrations through the calibration plot shown in Fig. 1 (Caliandro et al. 2013).

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Chiral Drug Separation by Membranes

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An enantiomer is one of two stereoisomers that are mirror images of each other and non-superposable. This feature of an enantiomer is called “chirality.”

Chirality is a very important key word in pharmaceutical industry, because more than half of pharmaceutically active ingredients are chiral (Sekhon 2010). In chiral drugs, one enantiomer shows desirable bioactivity, but the other enantiomer frequently does the less bioactivity or sometimes toxic side effects. Therefore, worldwide

sales of single-enantiomer drugs have been growing (Maier et al. 2001; Li and Haynie 2007).

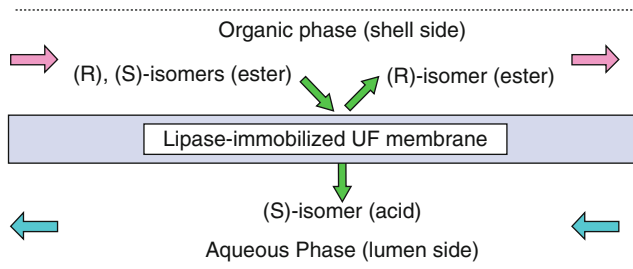
There are some techniques to prepare single-enantiomer drugs in pharmaceutical industry. One is chemical synthesis using chiral building blocks as starting materials. Another is asymmetric synthesis using enantioselective catalysts like chiral organocatalysts or biocatalysts. Optical resolution of enantiomers in a racemate is another important technique in chiral drug industry. The method of optical resolution can be applied to not only final racemic drugs but also racemic intermediates appeared in preparation steps.

We already have some techniques to separate one enantiomer from the other isomer: preferential crystallization, chiral chromatography, enantioselective extraction, enzymatic kinetic resolution, membrane separation, and so on. Among these techniques, membrane-based method has some advantages such as low energy demand, continuous operation, and easy scale-up. The important factor of membrane-based enantioselective separation is the way how to give the function of chirality recognition to membranes. In a supported liquid membrane, a liquid containing enantioselective carriers is impregnated into a porous support membrane (see the topic “► [Supported liquid membrane for enantioselective separation](#)”). In enantioselective solid membranes, chirality recognition exists in main polymer chain, chiral polymer branch, doped chiral selector, or cavity formed by molecular imprinting (see the topic “► [Enantioselective transport of amino acids by membrane operations](#)”).

Although the industrial application of membrane-based chiral separation has been very few until now, one successful example exists in chiral drug production. Diltiazem is a calcium channel blocker used for hypertension and angina treatment, and a lipase-immobilized membrane reactor was applied to the enantiomeric separation of chiral intermediate of this drug (Lopez and Matson 1997). In the separation process, a biphasic membrane system is used. Figure 1 shows the concept of enantiomeric separation in a biphasic membrane reactor using enzyme immobilized on the membrane surface. The

Chiral Drug Separation by Membranes,

Fig. 1 Concept of enantiomeric separation in a biphasic enzyme membrane reactor



immobilized enzyme on a membrane hydrolyzes preferentially one isomer ester in the organic feed phase, and the produced acid is extracted into the aqueous phase. In this system, reaction and separation occur simultaneously in/on membranes.

Membrane technology has a potential to improve the application of enzymatic reactions to the industrial scale production of chiral drugs. The recent progress of enzymatic membrane reactors was reviewed elsewhere (Rios et al. 2004).

The most important factor for successful optical resolution of enantiomers in a racemate is the design of a chiral selector fitting for the separation, because many drugs have complicated steric structures. One of the measures devised to deal with this problem is the implementation of combinatorial strategies (Maier et al. 2001). Large libraries of potential selectors are generated, and the systems with desirable properties are extracted from the libraries.

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Chlorination Process

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Chlorination process, in chemistry, is a halogenation reaction using chlorine. Because chlorine is a highly efficient disinfectant, chlorine is widely used in the treatment of water. In this case, the chlorination process is the addition of chlorine or chlorine compound. Aqueous free chlorine solutions contain three species in equilibrium, Cl_2 , HClO , and ClO^- . At present, it is generally accepted that the chlorination is closely related to the major chlorinating species in free chlorine solution and their concentration, both of which depend on the pH of the solution.

For membranes, the chlorination is the reaction of chlorine with membrane materials. The chlorine is widely used as the pretreatment agent during many kinds of membrane process because of their oxidability. However, this oxidizing chlorine can react with membrane, resulting in membrane failure. Usually, the hydrogen atom in the membrane is substituted by the chlorine atom. Many materials used for membrane fabrication contain active hydrogen. One of the most famous ones is polyamide, which is widely used for the fabrication of many kinds of membranes such as reverse osmosis membrane (RO), nanofiltration membrane (NF), gas separation membrane, pervaporation membrane, and forward osmosis

membrane (FO). The polyamide is easily to be chlorinated because the nitrogen atom on amide bond is susceptible to chlorine due to the electrophilic character of the carbonyl groups. The chlorination process of polyamide consists of the substitution of chlorine atom for hydrogen atom of amide bond, accompanied by weakening or destruction of the hydrogen bonds between polymer chains (Xu et al. 2013). This process consists of two steps: positive chlorine attachment to the amide unit at the O atom with lone electron pair followed by rapid rearrangement to the N-Cl (Avlonitis et al. 1992; Jensen et al. 1999; Challis and Challis 2010). For aromatic polyamide, the chlorination process consists of not only the substitution process but also the chlorination of aromatic ring through an intermolecular rearrangement after amide chlorination, known as the Orton rearrangement which involves the transfer of the N-chlorine atom from a side amino group to a phenyl ring forming various aromatic substitution products under acidic condition (Kwon et al. 2006a, b). Although the chlorination process could also be affected by various other factors (Gabelich et al. 2002, 2005; Tessaro et al. 2005; Murphy 1991), it is generally accepted that this chlorination is closely related to the major chlorinating species in chlorine solution and their concentration (Glater et al. 1981, 1982).

The chlorination usually causes serious degradation of membrane chemical structure, ultimately resulting in membrane failure. Therefore, developing novel membranes with high chlorine resistant property is very important for the wide application of membrane separation technology.

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Chlorine-Resistant Polymeric Membranes

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A chlorine-resistant polymeric membrane is mainly referred to a polymeric reverse osmosis (RO) desalination membrane that can withstand

exposure to chlorine and preserve its separation characteristics under such a harsh condition.

Currently, commercially available RO membranes are derived from two classes of polymers: cellulose acetate (CA) and aromatic polyamide (PA) (Li and Wang 2010). CA membranes are relatively low cost and tolerant to limited free chlorine. However, CA membranes suffer from some disadvantages such as a narrow operating pH range (4.5–7.5), susceptibility to biological attack, structural compaction under high pressure, and low upper temperature limit. On the other hand, PA thin film composite (TFC) membranes feature thin highly selective interfacially polymerized layers, which exhibit superior flux and salt rejections, wider operating temperature and pH range, and higher stability to biological attack, as compared with CA membranes (Park et al. 2008). Thus, PA TFC membranes used in RO are most preferred by the desalination industry. However, PA membranes encounter significant drawbacks in desalination processes, namely, membrane degradation under continuous exposure to trace amount of chlorine and deterioration of their performances.

Chlorine is the most common industrial oxidizing biocide in water treatment that is used for disinfection of domestic water and for the removal of tastes and odors from water. It is also typically used in RO treatment processes in order to control microorganisms that biofoul and clog the membrane. Consequently, water to be purified is often chlorinated, to disinfect it and ultimately inhibit biofouling of the membranes, and then dechlorinated before being fed to membrane desalination units. After passing through the membranes, the water is then rechlorinated before being sent to the distribution network. However, this requires additional equipments and chemicals and increased operating cost for the plant, accordingly.

When chlorine gas is added into water, it is hydrolyzed to form hydrogen ion, chloride, and hydrochlorous acids. The hydrochlorous can be further ionized to produce hypochlorite ions according to the following reactions (Geise et al. 2010):



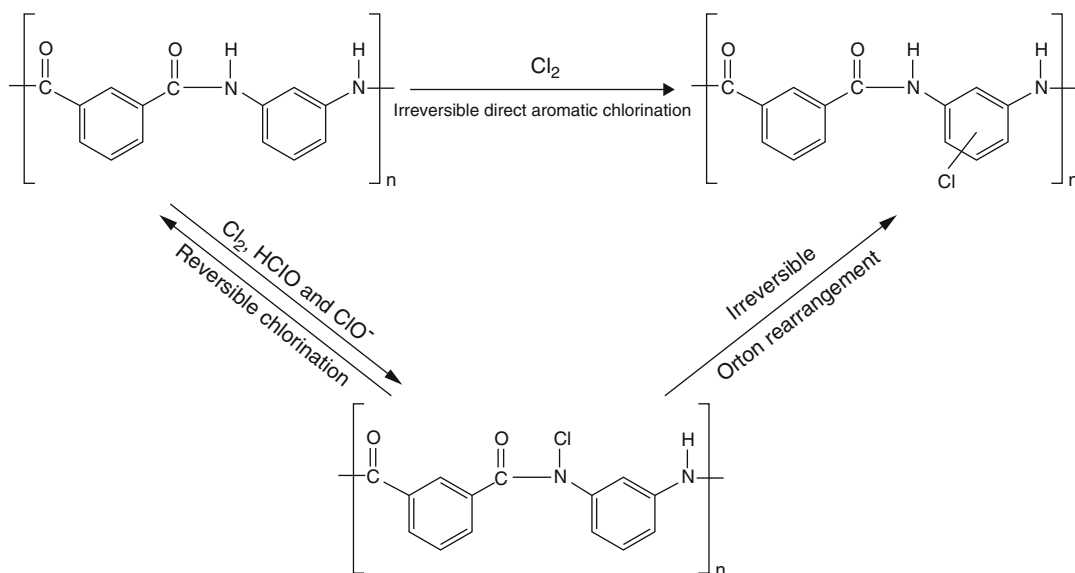
Cl_2 , HOCl , and OCl^- are in equilibrium, and depending on the pH, different distributions of aqueous chlorine species are observed (Deborde and von Gunten 2008). The established chlorinating strength of these species is $\text{Cl}_2 \sim \text{HOCl} > \text{OCl}^-$ (Soice et al. 2003).

The amide nitrogen of the membrane is highly vulnerable to chlorine attack because of electron-withdrawing effect of carbonyl group. Upon exposure to free chlorine, N-H group is chlorinated to N-Cl group which can reversibly form the initial amid by treatment with reducing agents. The aromatic rings are also susceptible to attack by chlorine because it is an electron-rich region. Two possible chlorination mechanisms are proposed for aromatic rings, i.e., direct chlorination of the aromatic ring and Orton rearrangement, which involves initial chlorination of amid nitrogen followed by an intermolecular rearrangement, forming various aromatic substitution products (Fig. 1) (Raval et al. 2010).

According to the chlorination mechanisms, chlorine resistance of PA membranes largely depends on the chemical structures of the diamine components used. Aliphatic PA reversibly reacts with chlorine to yield N-chlorinated amide. Tertiary PAs are inactive towards oxidative chlorine. The Orton rearrangement takes place only when amide linkage is directly connected with benzene ring. Generally, the chlorine resistance increases in the order of PA synthesized from aromatic, cycloaliphatic, and aliphatic diamines, respectively.

Thus, the following modifications can be considered as potential strategies to enhance the chlorine resistance of PA membranes (Geise et al. 2010):

1. Replacing chlorine-sensitive amidic hydrogen on the amide linkages with other moieties, e.g., methyl ($-\text{CH}_3$) or phenyl ($-\text{C}_6\text{H}_5$)



Chlorine-Resistant Polymeric Membranes, Fig. 1 Proposed mechanism of chlorination of aromatic PA (Reprinted from *Desalination*, 250, Raval HD, Trivedi JJ, Joshi SV, Devmurari CV, Flux enhancement of thin film

composite RO membrane by controlled chlorine treatment, 945–949, Copyright (2010) with permission from Elsevier)

2. Replacing the aromatic ring bonded to the amide nitrogen with aliphatic chain or cyclics
3. Prevention of Orton rearrangement by adding protective groups at the possible chlorination sites on the aromatic rings

Other than PA, polysulfone has much better chlorine resistance as it has stronger chemical bonds. However, due to hydrophobic nature of polysulfone, introduction of controlled levels of hydrophilic groups, e.g., $-\text{SO}_3\text{H}$, while retaining its physical properties is necessary for polysulfone RO membranes. The polymer chain cleavage and side reactions, which can make it difficult to control the degree of sulfonation and molecular weight and consequently drop the mechanical and the thermal properties of polymer, can occur in the post-sulfonation method. The direct synthesis of the functionalized polysulfone from a sulfonated monomer is found to be more advantageous since the associated challenges can be avoided (Park et al. 2008).

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Chloromethylation and Amination of Polymers (for AEM)

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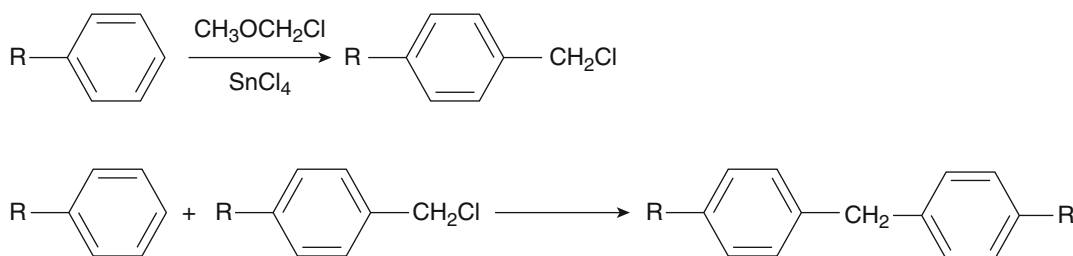
Chloromethylation (generally haloalkylation) of polymeric membranes followed by an amination reaction has been widely used for preparation of anion exchange membranes (AEMs). Significant efforts have been made to prepare AEMs from insoluble polymeric films such as polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). Such AEMs are typically prepared by grafting vinyl monomers such as styrene onto polymeric films and subsequent chloromethylation and amination modifications. Also, soluble polymers such as polystyrene (PS), polyether sulfone (PES), polyether ketone (PEK), or their blends or block copolymers have been widely used for preparation of AEMs. In such case, charged moieties can be introduced to the dissolved polymer via chloromethylation and amination reactions, either prior to the casting of polymer or after the casting into a film. Posttreatment, i.e., cross-linking of membranes, is often required to improve the chemical stability of AEMs prepared from soluble polymers (Xu 2005).

Chloromethyl groups can be introduced via Friedel-Crafts mechanism typically by reacting polymer with a chloromethylating agent, such as chloromethyl methyl ether ($\text{CH}_3\text{OCH}_2\text{Cl}$) or chlorotrimethylsilane ($\text{C}_3\text{H}_9\text{ClSi}$), using a metallic chloride (e.g., FeCl_3 , ZnCl_2 , or SnCl_4) as catalyst. Cross-linking of benzene rings with methylene bridges is encountered as a side reaction which would result in lower ion exchange capacity of final product according to the reaction presented in Fig. 1 (Jones 1952):

Alternatively, chloromethylation of polymers can be carried out using reaction mixtures which produce chloromethyl methyl ether in situ. These reaction mixtures are also known as chloromethylating complexes and may be, for example:

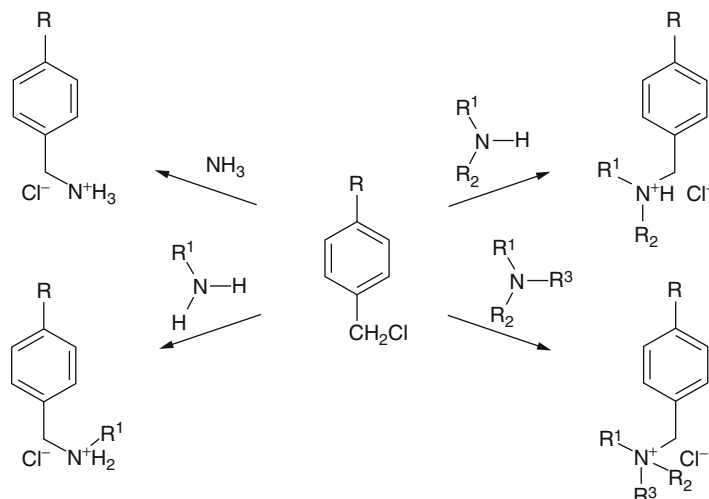
- Mixtures of paraformaldehyde and hydrochloric acid
- Mixtures of formaldehyde polymers and aluminum chloride
- Mixtures of methylal, thionyl chloride, and catalyst
- Mixtures of methylal, sulfonyl chloride plus chlorosulfonic acid, or chlorosulfonic acid only
- Mixtures of methylal, chlorosulfonic acid, and an oxygen-containing polar liquid

Among these complexes, the most commonly used are the ones that contain chlorosulfonic acid.



Chloromethylation and Amination of Polymers (for AEM), Fig. 1 Chloromethylation and methylene bridge crosslinking of polymers

Chloromethylation and Amination of Polymers (for AEM),
Fig. 2 Amination reaction of chloromethylated polymers



The reaction can be represented as (Boutier et al. 1980):



Positively charged groups are introduced to the chloromethylated polymer via amination reaction. The functional group of the AEMs can be weakly basic, such as primary, secondary, or tertiary amino groups which are obtained via reaction of chloromethylated polymer with ammonia or with primary or secondary amines, respectively. The amination reaction with tertiary amines, known as quaternarization, leads to AEMs with strongly basic functional groups (quaternary ammonium) (Helfferich 1995) (Fig. 2).

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Chromium Transport Through Ion Exchange Membranes

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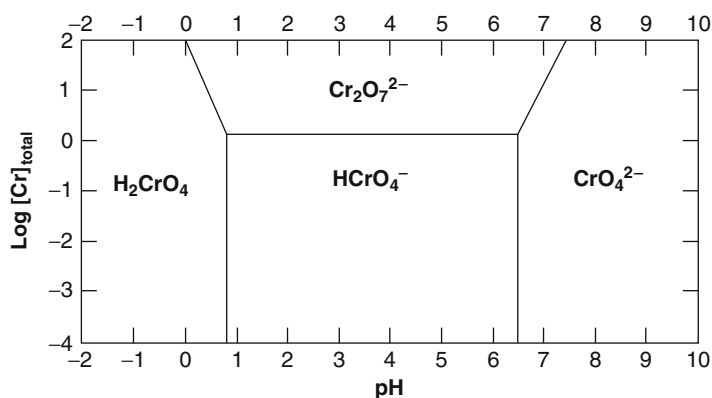
Occurrence and Removal of Hexavalent Chromium from Polluted Waters

The widespread use of chromium in industrial applications such as leather tanning, metallurgy, electroplating processes, and so forth has caused chromium contamination of surface and groundwaters (Pagilla and Canter 1999; Lin 2002; Rengeraj et al. 2001). Public concerns arise as a result of the sufficient evidence of chromium (VI) carcinogenicity in humans and the bioaccumulation into flora and fauna (IARC 1990; Kimbrough 1999).

Conventional processes reduce Cr^{6+} to Cr^{3+} , which is less toxic, less soluble, and less mobile than Cr^{6+} . Trivalent chromium is then converted to the hydroxide form and removed after precipitation (Hashim et al. 2011). Other technologies have been reported in literature as feasible

Chromium Transport Through Ion Exchange Membranes,

Fig. 1 Speciation diagram of Cr^{6+} in aqueous solution (Bringas et al. 2006a)



alternatives to achieve the removal and recovery of hexavalent chromium from wastewaters: adsorption and ion exchange (Mohan and Pittman 2006; Rivero et al. 2004), membrane processes (Bohdziewicz 2000) and separation processes based on the use of selective liquid membranes, especially emulsion liquid membranes (ELMs) (Salazar et al. 1992) supported liquid membranes (SLMs) (Kentish and Stevens 2001), non-dispersive solvent extraction (NDSX) (Bringas et al. 2012), and the emulsion pertraction technology (EPT) (Bringas et al. 2006a).

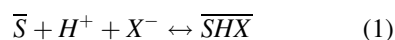
while in the acid range ($1 < \text{pH} < 7$), the coexistence of hydrogen chromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is expected. Therefore, the extraction of Cr^{6+} takes place through an anion-exchange mechanism, and thus, solvating and basic extractants are required.

The extraction of chromium by solvating extractants is based on the formation of an organic intermediate by the interactions between an electron donor (usually a phosphinic or a phosphoric moiety) and an electron acceptor (usually a proton) as shown by the following reaction which occurs in acid media:

Formulation of Selective Liquid Membranes for Hexavalent Chromium Removal

The main characteristics of the compounds to be employed as selective carriers in the formulation of selective liquid membranes in industrial applications are as follows: (i) high selectivity toward the target species, (ii) minimum extraction capacity of competing compounds, (iii) ease of regeneration, (iv) high solubility in low-cost solvents, (v) long-term stability, (vi) low cost, and (vii) not exhibiting toxic and carcinogenic properties.

Figure 1 shows the distribution of hexavalent chromium species in aqueous solution as a function of pH and the total chromium concentration (Bringas et al. 2006a). It is noticed that at basic pH values, the major species is chromate (CrO_4^{2-}),

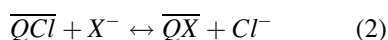


where $\bar{S}$ is the solvating carrier and X^- represents the target species.

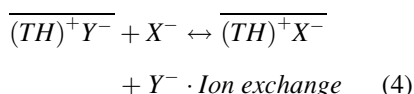
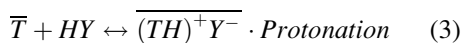
The commercial solvating extractants that employed the most on the removal of hexavalent chromium are TBP (tributyl phosphate marketed by Lanxess) (Venkateswaran and Palanivelu 2005), Cyanex 921 (trioctylphosphine oxide, TOPO, marketed by Cytec Industries) (Alguacil et al. 2004), and Cyanex 923 (a mixture of four trialkylphosphine oxides marketed by Cytec Industries) (Alguacil et al. 2004).

Tertiary amines and salts of quaternary amines represent the most important groups of basic extractants employed in the extraction of hexavalent chromium being the extraction mechanism described by the following ion-exchange reactions:

Salts of quaternary amines (chloride form)



Tertiary amines



where $\overline{QCl}$ is the chloride salt of a quaternary amine, $\overline{T}$ is a tertiary amine, and HY is a mineral acid.

Aliquat 336 (N-methyl-N,N-dioclyoctan-1-ammonium chloride marketed by BASF) (Bhowal et al. 2012) and Alamine 336 (mixture of tertiary amines with C₈ and C₁₀ groups marketed by BASF) (Bringas et al. 2006b) are the most reported commercial quaternary and tertiary amines employed in the removal of hexavalent chromium species.

Removal of Hexavalent Chromium from Polluted Groundwaters by the EPT Technology

Bringas et al. (2006a, b, 2007) reported the methodology for the optimal design of selective liquid membrane processes as efficient alternatives for the separation and selective recovery of hexavalent chromium from polluted groundwater generated by effluent leaking from surface deposition of industrial wastes. Furthermore, other competitive anionic species (mainly sulfate and chloride anions) were also present in the groundwater due to the specific location being close to the shore. The process should be designed to (i) reduce the chromium concentration in the polluted water below the disposal limit (0.5 mg L⁻¹) and (ii) obtain a concentrated chromium solution (>20 g L⁻¹) with negligible concentrations of sulfate and chloride anions. The design methodology is briefly illustrated in Fig. 2.

1.FUNDAMENTALS		
Problem Statement - Effluent characterisation - Objectives	Selection of Extraction (EX) and Back-Extraction (BEX) Agents - Proposal of EX and BEX reactions - Kinetic or equilibrium Patten - Obtention of the equilibrium/kinetic parameters	MBSX Technology Selection - Process configuration - Operational conditions
2. TECHNICAL EVALUATION		
Kinetic Analysis of the Separation - Concentration Process - Process Viability - Analysis of the influence of the operation variables on the EX and BEX kinetics		Mathematical Modeling of the Separation - Concentration Process - Mass transfer hypothesis - Solute mass balances in the different fluid phases - Mass transfer coefficients - Model validation
3. PROCESS DESIGN		4. ECONOMICAL EVALUATION
- Removal and recovery requirements (Constraints) - Preliminary capital cost definition (Objective Function) - Proposal of design alternatives (Network Superstructures) - Mathematical modeling of the network superstructures (Optimization Model) - Application of the mathematical optimization techniques to select the alternative with minimum total cost		Detailed cost evaluation of the selected alternative - Capital cost evaluation - Operation cost evaluation - Analysis of the investment recovery

Chromium Transport Through Ion Exchange Membranes, Fig. 2 Design methodology of selective liquid membrane processes

Synthetic solutions that simulate the anionic composition of the real groundwater [Cr^{6+}] = 500–1,300 mg L⁻¹, [SO_4^{2-}] = 900–3,000 mg L⁻¹ and [Cl^-] = 300–1,000 mg L⁻¹, were employed as feed solutions. The pH of the feed solution was adjusted to 1.5 using H_2SO_4 . The organic solution was formulated as follows: 10 % (v/v) of Alamine 336 as the anionic extractant, 3 % (v/v) of Pluronic PE 3100 as surfactant, and Isopar L fluid as solvent. The emulsion was prepared by dispersing the stripping solution (NaOH 3–6 mol L⁻¹) in the organic phase at a volume ratio organic/stripping = 4/1.

After defining the separation system, the experimental and theoretical description of the extraction equilibria was performed following the guidelines reported in Fig. 2. In general, extraction systems involving ionic species are generally thought to reach chemical equilibrium at the interface, and thus equilibrium models of the chemical reactions are proposed. Table 1 reported the

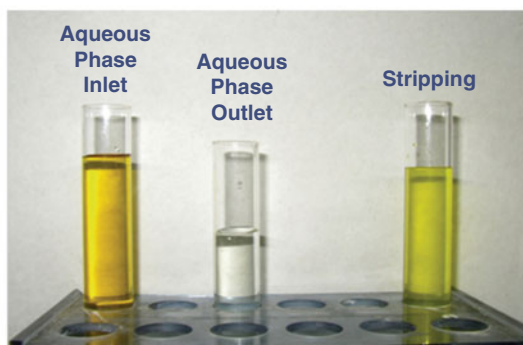
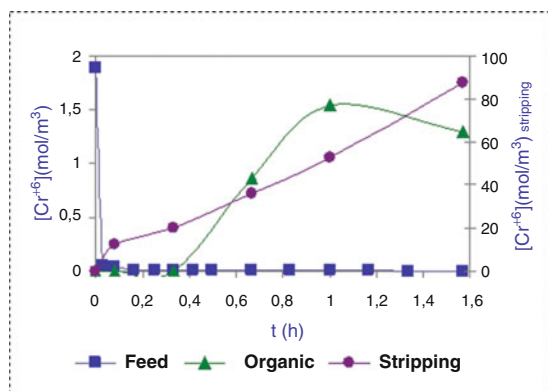
extraction mechanism and the equilibrium parameters for the multicomponent system, Alamine 336/chromium/sulfate/chloride.

The emulsion pertraction technology (EPT) which combines the advantages of ELM, i.e., high efficiency due to large surface area for mass transfer, and SLM, i.e., extraction and stripping are performed in one step without dispersion of the organic phase into the aqueous feed phase, was selected as the most suitable configuration of the selective liquid membrane technology. More details about the technology can be found elsewhere (Bringas et al. 2006a; Bringas and Ortiz 2014). Kinetic experiments were performed in a laboratory experimental setup containing a membrane contactor Liqui-Cel[®] Extra-Flow 2.5 × 8 with fiber X-30 that provides an effective membrane area of 1.4 m². Figure 3 shows the evolution with time of the chromium concentration in the different fluid phases (feed, organic, and stripping) and a

Chromium Transport Through Ion Exchange Membranes,

Table 1 Extraction mechanism and equilibrium parameters

Extraction reaction	Equilibrium parameter
$\text{HCrO}_4^- + \text{H}^+ + \text{R}_3\text{N} \rightleftharpoons (\text{R}_3\text{NH})\text{HCrO}_4$	$K_1 = 4.83 \text{ mol}^{-2} \text{ m}^6$
$\text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ + 2\text{R}_3\text{N} \rightleftharpoons (\text{R}_3\text{NH})_2\text{Cr}_2\text{O}_7$	$K_2 = 0.741 \text{ mol}^{-4} \text{ m}^{12}$
$\text{HSO}_4^- + \text{H}^+ + \text{R}_3\text{N} \rightleftharpoons (\text{R}_3\text{NH})\text{HSO}_4$	$K_3 = 1.37 \cdot 10^{-3} \text{ mol}^{-2} \text{ m}^6$
$(\text{R}_3\text{NH})\text{HSO}_4 + \text{Cl}^- \rightleftharpoons (\text{R}_3\text{NH})\text{Cl} + \text{HSO}_4^-$	$K_4 = 1.52$



Chromium Transport Through Ion Exchange Membranes, Fig. 3 Qualitative and quantitative evolution of the chromium concentration in the fluid phases (Feed solution: flows in continuous mode; Emulsion: recirculated)

photograph of the fluid phases at the end of the experiment. Similar extraction and back-extraction results were reported for sulfate and chloride anions (Bringas et al. 2006a).

The kinetic results confirmed the high selectivity of the carrier Alamine336 toward chromium species. The total chromium concentration decreased from 500 mg L⁻¹ at the module inlet to 0.8 mg L⁻¹ at the module outlet in one pass when the residence time in the module is 0.014 h. The chromium concentration in the stripping phase reached an average value of 14.6 g L⁻¹ after 1.3 h, and thus, a concentration factor of 18,733 was reached before depletion of the stripping reagent. From the analysis of the results obtained for the competitive species, it was concluded that the back-extraction process was not selective because all the species were totally back-extracted from the organic phase. For this reason the selectivity had to be controlled in the extraction step.

The kinetic analysis was completed with the proposal of the multicomponent separation mathematical model of the EPT process with the corresponding design parameters: (i) mass transport coefficients in the aqueous feed phase boundary layer (k_L), in the membrane (k_m), and in the organic phase stagnant layer ($k_o \cdot A_v$) for the different species involved in the separation-concentration process (see Fig. 4)

and (ii) the equilibrium parameters of the extraction reactions reported in Table 1. The model described satisfactorily the kinetics and selectivity of the separation-concentration EPT process under a wide range of operational conditions and served as a tool to perform the optimal design of the separation process (Bringas et al. 2006a).

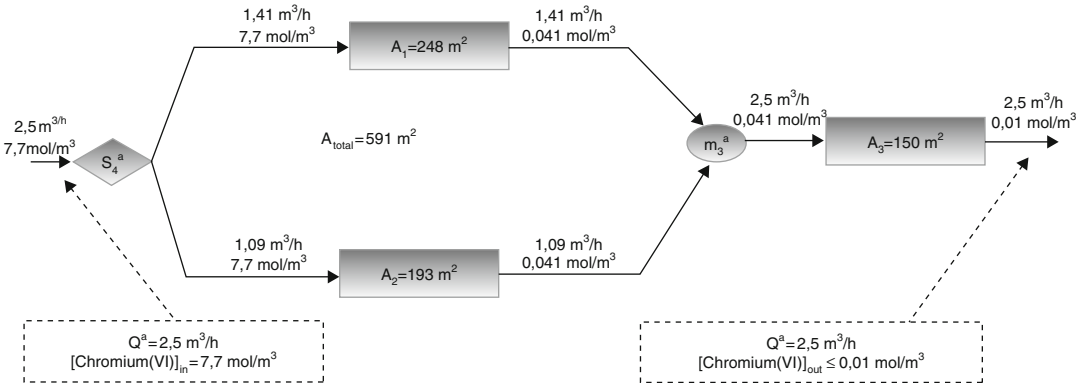
Finally, a novel design methodology based on the application of mathematical optimization was developed in order to determine the optimal EPT process configuration able to achieve, at minimum cost, the separation and concentration objectives, (i) the contaminant removal up to the required concentration level ($[\text{Cr}^{6+}] < 0.5 \text{ mg L}^{-1}$) and, (ii) the selective contaminant recovery to obtain a concentrated solution that can be reused elsewhere ($[\text{Cr}^{6+}] 20 \text{ g L}^{-1}$). The different design alternatives were represented by means of network superstructures that were modeled through the developed EPT mathematical model, generating optimization problems that were solved following global optimization techniques (Bringas et al. 2007).

The procedure was illustrated for the treatment of an incoming groundwater stream with a known flow rate of 2.5 m³ h⁻¹ and a chromium concentration of 400 mg L⁻¹ (7.7 mol m⁻³). Comparison of the results obtained from the analysis of the different design alternatives concluded that a

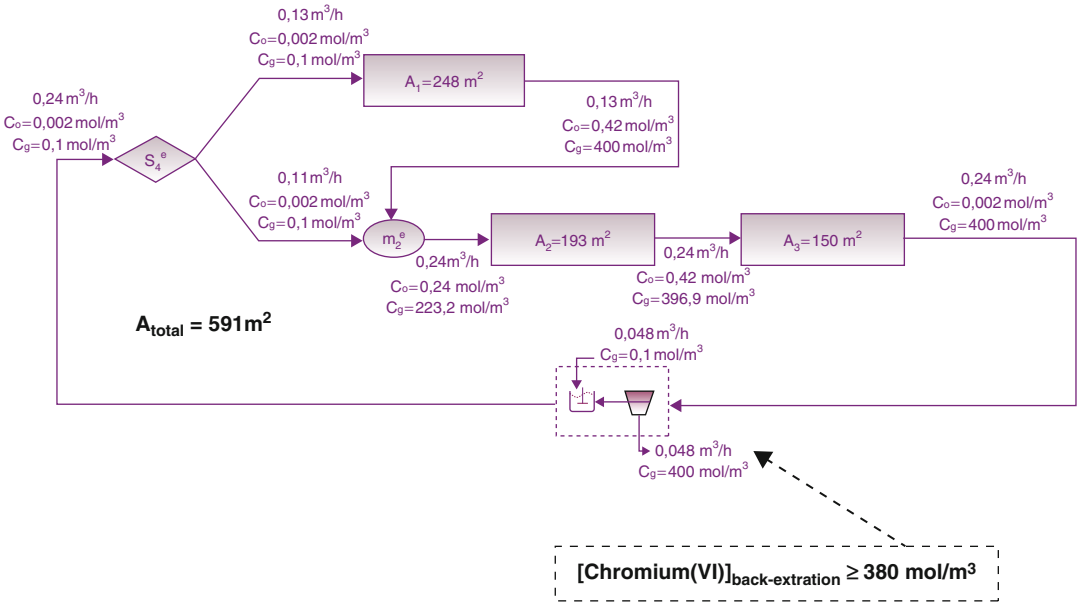
Chromium Transport Through Ion Exchange Membranes,

Fig. 4 Values of the mass transport coefficients in the EPT mathematical model

Parameter			Value	Obtaining
Mass Transport Coefficients	Aqueous Phase Stagnant Layer (k_{Li})	$K_{L,Cr}$	$0.217 \cdot (Q_2^{1/3}) (\text{m/h})$	Calculated
		$K_{L,Sulphate}$	$0.234 \cdot (Q_2^{1/3}) (\text{m/h})$	
		$K_{L,Chloride}$	$0.317 \cdot (Q_2^{1/3}) (\text{m/h})$	
		K_{L,H^+}	$0.256 \cdot (Q_2^{1/3}) (\text{m/h})$	
	Membrane (k_m)	$K_{m,Cr}$	$1.2 \cdot 10^{-3} \text{ m/h}$	Parametric Estimation
		$K_{m,Sulphate/Chloride}$	$1.5 \cdot 10^{-3} \text{ m/h}$	
	Organic Phase Stagnant Layer (k_o)	$K_o \cdot A_v$	$2.94 \cdot 10^4 \text{ h}^{-1}$	



Chromium Transport Through Ion Exchange Membranes, Fig. 5 Optimal process configuration for the aqueous feed solution



Chromium Transport Through Ion Exchange Membranes, Fig. 6 Optimal process configuration for the emulsion phase

network configuration with three treatment modules combined in series and parallel and with a total membrane area of 591 m² was the most suitable process configuration to comply, at minimum cost, with the concentration specifications in the outlet streams. Figures 5 and 6 show the optimal networks for the aqueous feed solution and the emulsion phase, respectively.

Future Directions

Future development will require research and development activities in the following areas:

1. Evaluation of the operation cost (energy and material costs) to be considered in the formulation of the objective function

- employed to determine the optimal process network
2. Analysis of the long-term performance of the separation process to evaluate the stability of the selective carrier which guarantees the process economic viability
3. Rigorous evaluation cost of the optimal process network

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Citric Acid Recovery by Electrodialysis

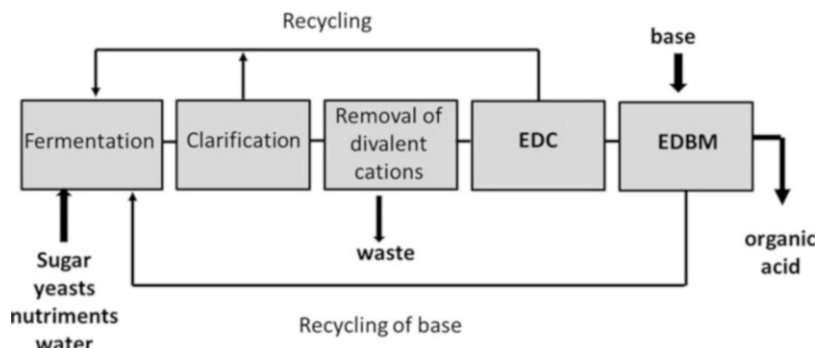
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Carboxylic acids such as lactic, succinic, gluconic, citric, and tartaric are widely used in food processing, detergent manufacture, and biodegradable plastic production (Bailly et al. 2001). Their production at the industrial scale is mainly achieved by mean of fermentation from molasses, starch hydrolysates, or sugars. Traditional processes to obtain these carboxylic acids consist on the precipitation of both the acids and their salts, so they can be isolated from the rest of the components of the raw material. Then, they are placed in an acid medium (sulfuric acid) to generate the acid form. A latter concentration step is carried out by evaporation followed by a crystallization. This generates large volumes of effluents with high salt contents. For example, typical yields of 1 kg of

Citric Acid Recovery by Electrodialysis,

Fig. 1 Scheme of a process of carboxylic acid production from fermentation. (EDC) concentration ED step, (EDBM) ED with bipolar membranes



citric acid are obtained per 2 kg of gypsum which is very difficult to dispose (Bialek and Ollis 1986). In order to reduce this environmental impact, the design of alternative production scheme was investigated. Extraction, adsorption, and membrane technologies, like electrodialysis (ED), were proposed to replace precipitation (Novalic et al. 1995). A complete scheme for carboxylic acid recovery is depicted in Fig. 1.

For EDC step of citric acid salts to the three dissociation constants of citric acid, the conductivity is mainly influenced by the pH value and the concentration. More ion dissociation leads to formation of further citric-acid-charged complexes in the solution which in turn causes electrical resistance reduction of the solution. The maximum ion density and consequently the minimum electrical resistance of the solution is obtained at pH 8 (Novalic et al. 1995). The EDBM step, which is water splitting by membrane electrodialysis, provides an attractive complement to the fermentation technology by removing the product acid while simultaneously providing an equivalent amount of base for use in adjusting the pH in the fermentor (Fig. 1). Moreover, the produced citric acid is usually at a relatively high concentration (0.5 M) so that the subsequent purification via crystallization or other techniques is relatively inexpensive (Xu and Yang 2002).

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Cleaning Cycle of Fouled Membranes

Hongyu Li

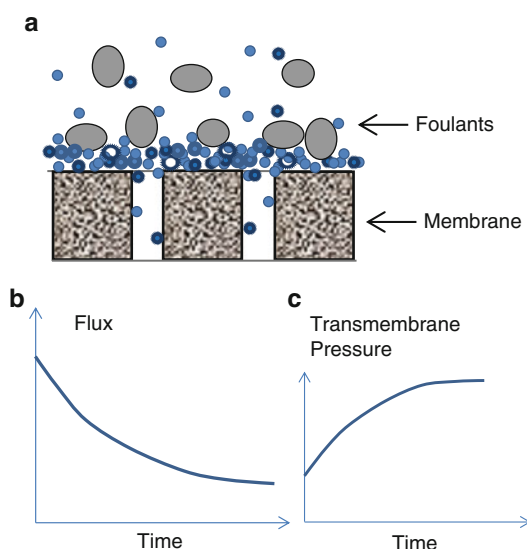
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Membrane Fouling

Membrane fouling is an unavoidable process in almost all industrial membrane applications. It refers to the deposition of foulants (solutes or particulates) on the membrane surface and/or inside the membrane pores during membrane separation process. Figure 1a demonstrates a typical membrane fouling structure in ultrafiltration (UF) and microfiltration (MF) systems.

The consequence of membrane fouling is the deterioration of membrane separation performance, which can manifest in two possible ways:

1. Decreased productivity, which can be observed in the reduction of permeate flux at a constant



Cleaning Cycle of Fouled Membranes, Fig. 1 Structure of membrane fouling layer in UF or MF filtration system (a) and observation of flux (b) or transmembrane pressure changes during fouling process

pressure operation mode (Fig. 1b) or increase in transmembrane pressure in a constant flux operation mode (Fig. 1c).

2. Changed separation efficiency in terms of selectivity of particular species, due to the altered surface characteristics by the buildup of fouling layer such as pore size, surface charge, or hydrophobicity.

While membrane fouling is unavoidable in most cases, the degree of fouling can be managed by using:

- (a) Appropriate membranes for a particular application
- (b) Appropriate pretreatment processes for the feed before the membrane process
- (c) Well-managed hydrodynamics in the membrane system and optimized operation system incorporating membrane cleaning process

Considerations for Membrane Cleaning

Understanding the properties of the feed including the main components as the potential foulants on

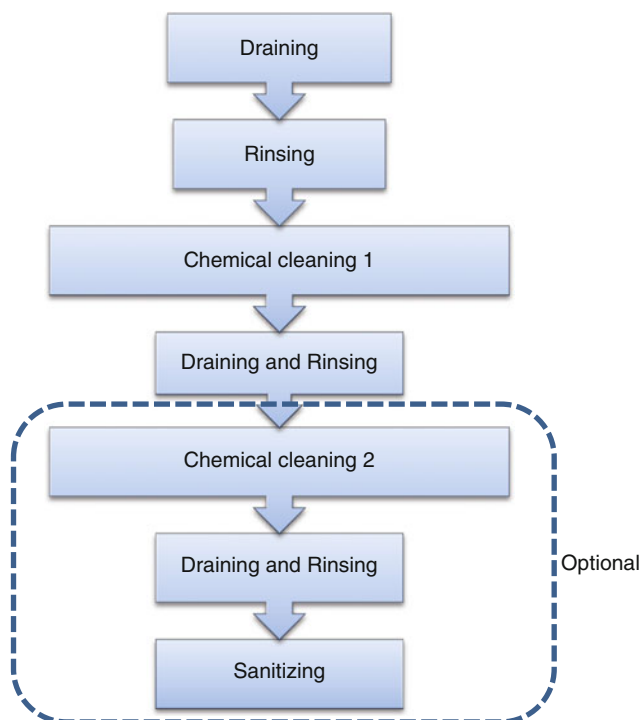
the membrane as well as understanding the fouling mechanisms of operation conditions such as applied pressure, shear rate on the membrane surface, operational temperature, the length of membrane operation, and the degree of membrane fouling could provide great insight for the selection of membrane cleaning protocols and the cleaning frequencies.

For example, microfiltration (MF) and ultrafiltration (UF) membranes used in the dairy industry for concentration of milk or removal of bacterial and spores would encounter components in the feed and potential foulants such as proteins as whey and casein, carbohydrates, fats, and minerals. Membranes used in reverse osmosis (RO) of seawater may experience organic fouling caused by humics, fulvic acid, carboxylic acid, and extracellular polymeric substances (EPS) as well as biofouling, which may involve adsorption of organic matter to membrane surface, continuous adhesion of microorganisms, growth of adhered cells, or subsequent formation of biopolymer matrix. Inorganic fouling or scaling initiated by supersaturation of minerals on the membrane surface is also common in RO, UF, and membrane distillation (MD) processes.

Operation conditions of a membrane separation process also affect properties of foulant accumulated on the membrane. For example, higher transmembrane pressure in RO, UF, and MF processes leads to higher convection of foulants to the membrane surface, resulting in a higher level of concentration polarization and eventually fouling. Higher pressure can also cause compaction of already formed foulant layer and make it more difficult to clean. Higher shear near the membrane surface causes higher back transport of foulant away from the concentration polarization layer and could reduce the formation of fouling layer on the membrane. On the other hand, the back transport of bigger foulants occurs preferentially over smaller ones, which could lead to the formation of foulant layer with smaller species, which could contribute in higher resistance and is more difficult to remove. Operation at higher temperature should lead to higher flux; however, denaturation of certain species such as protein could also lead to more difficulty in cleaning foulant layers.

Cleaning Cycle of Fouled Membranes,

Fig. 2 Stages of a cleaning cycle



Membrane Cleaning Process

The aim of membrane cleaning is to disrupt and remove foulants from the membrane surface and restore the membrane separation capability. The process is normally comprised of steps (as shown in Fig. 2) including draining of the feed solution from the membrane system, rinsing of loosely bound foulants with clean water, and chemical cleaning through breaking the cohesive and adhesive bonds between the foulants and between the foulant and the membrane. Sequential cleaning with a second chemical is also common for routine operations over repeated filtration and cleaning cycles over a long period.

Draining and rinsing before application of chemicals in membrane cleaning is very important. Without these steps, the majority of the chemical cleaner would be consumed by the residual feed instead of the foulants on the membrane surface and thus achieve low cleaning efficiency.

Rinsing should normally be conducted at the same temperature as cleaning to avoid compaction of foulants and normally takes 5–20 min.

During the chemical cleaning process, sufficient contact between the cleaning agent and the foulant is probably the rate limiting factor for cleaning reactions. This requires efficient transport of chemical to the foulant sublayer and rapid removal of the dislodged foulant away from the membrane. Appropriate chemicals should be selected that can attack the structure of foulant by cleavage of bonds within the foulant molecules and between the foulant aggregates, or solubilize the foulant deposits.

Chemicals for Membrane Cleaning

Selection of right chemical is most important for achieving an efficient cleaning reaction and process. Common chemicals used for membrane

Cleaning Cycle of Fouled Membranes, Table 1 Common chemicals used for membrane cleaning and their cleaning mechanisms

Chemical type (and simple chemical examples)	Cleaning mechanisms and applications
Caustic or alkaline (NaOH, KOH)	Hydrolysing, cleavage of disulphide bonds for protein aggregates for cleaning of protein foulants Saponificate fats and lipids Dissolve inorganic and organic foulants
Acidic (HCl, H ₃ PO ₄ , nitric acid, citric acid)	Solubilization and chelation for scale compounds and metal oxides Dissolving precipitates
Enzymatic cleaning (Protease, Lipase based commercial enzymes)	Cleave specific peptide bounds in the proteins Operate at conditions when enzyme activity was highest
Surfactants or wetting agents (Anionic, cationic surfactants)	Lower the surface tension of cleaning solution and increase solubility Displace foulants and prevent redeposition Improve contact between cleaning chemical and deposits
Oxidants (Free chlorine, NaOCl)	Oxidize foulant and increase hydrophilicity
Sanitizers and disinfectants	Used at the end of cleaning cycle or as part of the storage regime between uses

cleaning include alkaline or caustic chemicals such as sodium hydroxide used for hydrolysis and solubilize foulants, acids such as citric acid and nitric acid with solubilization function. Surfactants and detergents are also frequently used for emulsifying, dispersion, and surface condition purposes as shown in Table 1. Many membrane companies provide cleaning advice and procedures to their membrane products, some also have their own proprietary products. Many cleaning products are formulated with a mixture of chemicals that could include alkaline (or acidic), surfactants, and disinfectants.

Given their specific functions in cleaning mechanisms and the complexities of the feed and foulants, sequential cleaning, cleaning with one

type of cleaning agent followed by cleaning with the second chemical, can prove more effective in achieving higher overall efficiency. For example, acidic cleaners are often used in conjunction with alkaline cleaners to chelate calcium and magnesium ions that would otherwise form insoluble soap residuals. The acidification wash can also be applied to neutralize residual alkalinity and remove mineral deposits that may have formed during the alkaline cleaning or alkaline based enzyme cleaning.

Cleaning Conditions

Operating chemical cleaning at appropriate conditions such as circulation of the cleaning solution over the membrane surface provides mixing and shear force to the foulants from the membrane surface to the bulk.

With the selected chemicals and cleaning protocols, parameters such as concentration of cleaning agent, cleaning time, temperature, and hydrodynamic conditions during the cleaning process can all affect the overall cleaning efficiency. Chemical compatibility between the membrane and other filter components to the cleaning chemicals is also an important factor in selection of suitable cleaning chemicals. Membrane systems made of high chemical tolerances would allow greater freedom in selecting the composition, strength of cleaning solutions as well as the conditions for cleaning. On the other hand, milder cleaning conditions would have much less detrimental effect on the membrane integrity and life span as well as being more environmentally benign. Cleaning at higher temperature could lead to higher cleaning reaction and lower viscosity with high cleaning efficiency. However, optimized cleaning condition should be considered with the following factors in mind.

- Running costs in cleaning chemicals,
- Down-time,
- Membrane integrity over long period of time and
- Environmental impact for discharge of cleaning chemicals.

Summary

Membrane cleaning is an essential part of membrane operation system. Design and selection of cleaning protocol should start with the identification of potential foulants and the understanding of the membrane fouling process and mechanisms, followed by selection of appropriate chemical agents to the specific foulants. An effective cleaning process should start with proper draining of the feed and rinsing of the system prior to application of chemicals. Consideration of clean process design should include the membrane separation performance over many repeated cycles of fouling and cleaning, the effect on membrane integrity as well as overall operation and disposal costs.

The following reading materials are recommended for more information.

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membrane life while also minimizing expense and time.

Factors that influence the selection of membrane cleaning regime are listed in Table 1. Normally the chemical and temperature tolerance of membranes will be recommended or can be obtained from the membrane manufacturer. Inorganic membranes have a much higher tolerance of harsh chemicals and a higher temperature range than polymeric membranes.

The application with specific feed solution and operation conditions will dictate the foulants on the membrane and the strength of bonding between the foulant and foulant and the membrane. One example is membranes used in dairy application where the milk concentration would experience membrane fouling with protein as well as lactose and minerals. The cleaning of membranes used in dairy applications normally involves caustic cleaner in daily basis. On the other hand, membranes used in reverse osmosis (RO) would experience fouling by scale of calcium, ions, colloidal deposits, organic matter, and biological materials. The frequency of RO membrane cleaning ranges from once in a few month up to once a year.

An effective cleaning process should remove the foulants/deposits and other contaminants from the membrane surface and cassette feed channels and restore the membrane separation performance to a predictable, consistent level. This is usually evaluated by measurable parameters such as:

Cleaning Effectiveness

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Cleaning effectiveness refers to how useful a cleaning regime is in regard to a specific application. An effective cleaning protocol to one application may not be very useful in another situation. An effective cleaning regime must accommodate a variety of factors in order to maximize

Cleaning Effectiveness, Table 1 Factors and considerations for selection of membrane cleaning protocol

Factors	Consideration for clean
Membrane material (polymeric, inorganic)	Tolerance to chemical and temperature could affect membrane lifetime
Feed composition and the degree of fouling	Specific chemicals and regime to specific foulants and degree of fouling Frequency of cleaning relates to costs and membrane lifetime
Membrane module configuration (flat sheet, hollow fiber, spiral wound)	Amount of cleaning solution required and operation conditions of cleaning

(a) Clean water permeability

This can easily be estimated by measuring membrane flux of clean water at defined operation conditions, for example, at fixed pressure and temperature. Low recovery of clean water permeability indicates an insufficient cleaning process.

However, this parameter is not always reliable for evaluation of cleaning effectiveness. A good clean water permeability recovery does not always represent a total removal of foulants from membrane. In some situations, a partial removal of the residual foulant does not contribute significantly to clean water permeability, and the separation performance in subsequent operations could be exasperated due to the existing residual foulant.

(b) Analysis of flush solution after cleaning can also be used to indicate the presence of foulant in the system after cleaning.

Apart from these methods commonly applied in cleaning-in-place (CIP) applications that do not affect continued membrane usage and functioning, other techniques that require removal of membrane from module and sometimes destruction of membrane can also be applied for diagnostic procedure, including:

(c) Analysis of membrane surface properties, such as surface charge, contact angle, and elemental analysis of species as well as SEM imaging on the membrane, which can be used to observe the extend of the amount of residual foulants on the membrane.

separation performance. Cleaning efficiency is commonly measured by either the membrane flux recovery or resistance removal (Li and Chen 2010).

The flux recovery is estimated by the comparison of membrane water fluxes before fouling and cleaning and water flux after cleaning. The flux recovery can be estimated as

$$\text{Flux Recovery} = \frac{J_{wc}}{J_{wi}} \times 100 \% \quad (1)$$

where J_{wc} is the water flux after cleaning and J_{wi} is the water flux before the membrane was subjected to fouling.

The resistance removal can be estimated as

$$\text{Resistance Removal} = \frac{R_r - R_c}{R_r} \times 100 \% \quad (2)$$

where R_r is the membrane resistance before cleaning and R_c is the membrane resistance after cleaning. The membrane resistance is estimated with clean water flux of membranes at different stages of operation with

$$R = \frac{\Delta P}{\mu J} \quad (3)$$

where J is the water flux, ΔP is the transmembrane pressure of water flux measurement, and μ is the viscosity of water (at the temperature of water at the flux measurement).

This type of assessment involves measurements of membrane fluxes prior the filtration process, the initial water flux (J_{wi}), membrane flux at the end of filtration process (J_{wf}), membrane flux after rinsing (J_{wr}), and membrane flux after cleaning (J_{wc}).

Analytical methods can be used to evaluate the changes of membrane surface properties such as charge and contact angle before and after cleaning. Infrared and X-ray photoelectron spectroscopy of the cleaned membrane has also been used in identifying remaining foulants on the cleaned membrane.

A “cleaned” membrane subject to extensive extraction methods can reveal not only the amount of residual foulant on the membrane but also the composition foulants left on the membrane after cleaning. This information can be very useful to

Cleaning Efficiency

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Cleaning efficiency measures how well the cleaning process is in recovery of the membrane

formulate sequential cleaning strategies by using one agent to clean one part of the foulant and a second, more effective, agent in removing the remaining of the residual.

One example is the cleaning of membrane used in whey protein filtration. Through analysis of foulants extracted from the membranes before and after cleaning with gel electrophoresis (SDS-PAGE) technique for protein composition, it was revealed that the high molecular weight components in the foulant layer could be more easily cleaned than the smaller components. Sequential cleaning using NaOH for removal of large protein followed by HCl solution for cleaning of smaller molecules has shown consistent performance restoration over repeated cleaning cycles (Norazman et al. 2013).

Parameters Affect Cleaning Efficiency

Both the properties of cleaning solution (concentration, pH) and the operational condition (pressure, temperature, velocity, and cleaning time) could affect the outcomes of cleaning.

Generally speaking, conditions that favor the contact between the cleaning chemical and the reaction rate would be beneficial for efficient cleaning. For example, cleaning solution of higher concentration would have a higher rate of reaction with foulants, higher temperature improves reaction rate, and cleaning time relates to contact and reaction time. High circulation rates also lead to more turbulence and high shear rate which favors removal of dislodged foulants from the membrane. Low pressure could avoid redeposition of foulant.

However, practical experience suggests that for specific cleaning applications, the optimum cleaning conditions should be determined on considerations of limiting conditions of all those factors. For example, the integrity of membrane material and hosing material could be compromised at temperature above their tolerance level. Extensive circulation at high flow rate relates to higher energy cost.

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Cleaning-in-Place (CIP) Systems

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Cleaning-in-place (CIP) is a method of cleaning closed systems in industrial settings, such as interior surfaces of pipes, vessels, heat exchangers, process equipment, filters, membrane systems, and their associated fittings without disassembling.

Opposed to cleaning-in-place is disassembled cleaning, which refers to a method of cleaning that works by disassembling the closed systems and cleaning individual components (often manually) before assembly for continued usage. Many laboratory facilities and small-scale systems are commonly cleaned and disinfected this way.

For industry-scaled applications, with systems that require frequent internal cleaning and high level of hygiene, such as dairy processing, beverage processing, processing of food, bioprocesses, and pharmaceutical applications, automated cleaning-in-place provides great benefits of faster, safer, and reliable cleaning processes which is very important for industrial considerations.

The purpose of membrane cleaning is to remove foulants and deposits on the membrane surface and membrane pore structure to restore the

membrane separation capabilities that had been compromised by membrane fouling.

Many membrane foulants behave as cohesive solids ranging from soft macromolecular gels to hard mineral scales on the surface. Breakdown of these foulants may include dissolution or solubilization, disruption of cohesive interactions between aggregates within the deposit, or disruption of the adhesive forces that bind foulant particles/molecules to the surface.

The common practice of cleaning-in-place of membrane system often involves a combination of hydraulic and chemical cleaning in three distinctive steps:

1. Draining before cleaning. The membrane operation (e.g., filtration of milk) is stopped and the transmembrane pressure is released to allow relaxation and redistribution of the foulant into the feed stream. The feed solution is then drained.
2. Rinsing. This involves replacing feed with clean water in circulation at low pressure to flush and remove loose foulants from the membrane surface.
3. Chemical cleaning. This introduces the cleaning solution into the membrane system, allowing circulation at low pressure in order to break down foulant structure and increasing solubilization of foulant species from the membrane surface.

Selection of chemical cleaning agent should consider:

- Compatibility between the cleaning chemical and the membrane material and fitting components.
- The cleaning agent should be safe and does not pose as potential contaminants to the product.
- Disposal of the cleaning chemicals.

Selection of cleaning process operation condition should consider:

- Overall downtime from production
- Temperature tolerance of membrane material
- Cost of energy for cleaning

Common cleaning agents used by industry for CIP include acids, bases, enzymes, surfactants, disinfectants, and steam and gas sterilization (Mulder 1996), depending on the feed composition and severity of fouling.

Alkaline cleaners, particularly sodium hydroxide and potassium hydroxide, with their ability to dissolve protein molecules, fats, and other precipitated materials, have been used to clean membranes fouled with proteins.

Acidic cleaners include nitric acid, hydrochloric acid, and phosphoric acid, and better cleaning results with HCl for the membrane fouled with milk components have been reported. Acidic cleaners have potential for dissolving precipitates formed during the cleaning procedure.

Enzymatic cleaners have the unique benefits of being biodegradable and more environmentally friendly. Enzymatic cleaners possess great potential to remove proteinaceous matter from the membrane. Proteases are the most commonly used enzymatic cleaners with their function of hydrolyzing peptide bonds in the proteins which leads to the disassembly of protein (Petrus et al 2008). However, a major concern associated with enzymatic cleaning is the possibility of membrane fouling by the enzyme molecules employed in the cleaning process.

Surfactants can be used to improve the contact between the cleaning chemicals and the foulant, thus improving the reaction rate (Trägårdh 1989).

Quite often, better cleaning performance can be achieved by combining cleaning agents or sequential cleaning.

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Closed-Loop Cascade Diafiltration

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Closed-loop cascade diafiltration (Charcosset 2012) is used when the product to be recovered appears in the permeate of the first stage of a two-stage process. It is similar to ► [open-loop cascade](#) diafiltration but differs in that the permeate from the second stage is recycled and used as the diluant of the first stage. A schematic is shown below (Fig. 1).

The obvious advantage of this approach over the open-loop configuration is the reduced requirement for a fresh diluant. In principle, the product should have a low rejection coefficient in the first stage and a high rejection coefficient in the second stage.

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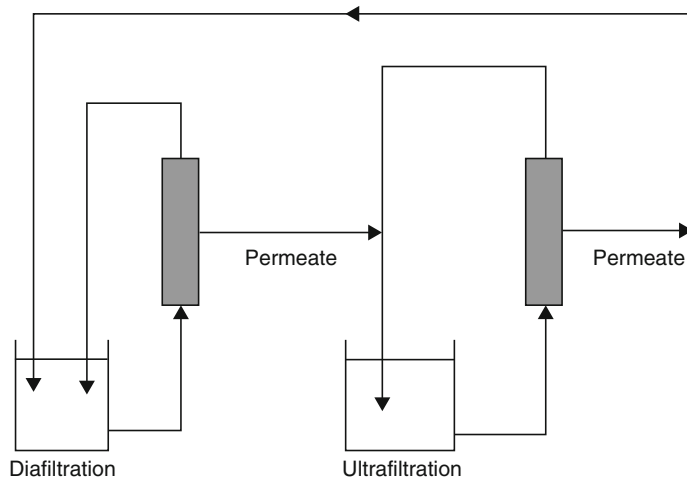
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Co (II) Ions Separation by Supported Liquid Membranes

► [Cobalt Removal and Recovery by Supported Liquid Membranes](#)

Closed-Loop Cascade Diafiltration,

Fig. 1 Closed-Loop Cascade Diafiltration



CO Inhibition to Pd-Based Membrane

► [Inhibition of Hydrogen Permeation Through Pd-Based Membranes by CO](#)

CO Selective Oxidation

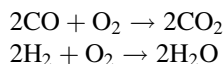
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Hydrogen purification is a critical technology for many chemical and petrochemical processes and power generation by PEM-FCs (proton exchange membrane fuel cells) as well. Carbon monoxide is, in fact, a poisoning or inhibitor for most catalysts such as the Fe_3O_4 one involved in ammonia synthesis or the platinum-based one used at a low temperature in PEM-FCs. In the latter case, in order to avoid cell performance degradation, carbon monoxide concentration must be kept below 10 ppm in the hydrogen feed streams.

CO selective or preferential oxidation is the primary method used for hydrogen deep purification (Avgouropoulos and Ioannides 2003), and different research groups (Manasilp and Gulari

2002; Souza et al. 2007; Bissett and Oh 2005; Woortsch et al. 2004; Sirijaruphan et al. 2004; Kotobuki et al. 2005) work on this topic. The involved reactions are:



Therefore, a catalyst active for CO oxidation in the presence of high concentrations of H₂, CO₂, and steam is required to avoid H₂ consumption, nor should it have a strong preference to the water-gas shift reaction since in these conditions of temperature and gas composition, the equilibrium gives ca. 0.5–2 %mole of CO.

Both alumina-supported Pt and Au catalysts have been found to be active for CO Selox (Luengnaruemitchai et al. 2004). Pt-based catalysts require high temperatures (about 170 °C) and a high feed molar ratio O₂/CO (about 1.5) for complete CO depletion, with a corresponding loss of selectivity (typically 34 %). Water vapor has a positive effect on these catalysts, increasing the conversion without changing the selectivity; instead CO₂ has a detrimental effect (Avgouropoulos et al. 2002). Au-based catalysts are more active than platinum catalysts at relatively low temperatures (<120 °C) but not so resistant toward deactivation by CO₂ and H₂O. Promoted Pt/Al₂O₃ catalysts (e.g., with Ru or Rh) have also been investigated. Values of ca. 15 ppm of CO in the reactor outlet are reported for a microreactor (Pt–Ru/α-Al₂O₃ catalyst) operated with a O₂/CO feed molar ratio of 1.5 and 4 (Delsman et al. 2004; Cominos et al. 2005). Whereas, values of CO less than 10 ppm were reported for a fixed bed reactor using a O₂/CO feed molar ratio of 2.5 (Dudfield et al. 2000). Other interesting active and very selective catalysts are CuO–CeO₂ mixed oxides (Avgouropoulos and Ioannides 2006; Zou et al. 2006); however, the presence of H₂O and CO₂ in the feed causes a significant decrease in their activity (Avgouropoulos et al. 2005).

Apart from the improvement of the catalyst, new reactor concepts are being studied. Monoliths present different advantages over particulate catalysts, including pressure drop reduction, ease of handling, structural robustness, and possibly

increased heat transfer. Interesting new engineering devices such as catalytic membranes and catalytic membrane reactors were investigated in a few papers for CO selective oxidation (Hasegawa et al. 2001, 2002; Bernardo et al. 2006). The concept of using Pt in zeolite catalysts was applied for this reaction by Watanabe et al. (1995; Igarashi et al. 1997). In a recent paper (Kotobuki et al. 2005), a significant improvement of CO conversion and selectivity with high Pt dispersion in the zeolite (ZSM-5) pores was demonstrated. Zeolites play host to noble-metal clusters for numerous catalytic applications, and well-defined clusters of narrow size distribution down to 1 nm have been obtained under suitable conditions (Pan et al. 1990; de Graaf et al. 2001). Investigations on the use of large-pore diameter zeolite such as Pt-loaded FAU-type membranes (Bernardo et al. 2006) show also the possibility of collocating a membrane reactor CO selective oxidation stage (operating at 200–220 °C and with a feed ratio O₂/CO = 1) after the low-temperature water-gas shift reactor in a reforming plant. One of the findings of this study was the possibility of improving CO removal by increasing the operating pressure.

A zeolite catalytic membrane provides catalytically active and nano-sized particles entrapped in a thin zeolite layer (a few microns thick), resulting in:

- Efficient reactant/catalytic phase contact, reducing bypassing and misdistribution generally shown in a packed bed
- Short and narrow distributed contact time
- Hot spot control that is beneficial since a local temperature increase can lead to promotion of reverse water-gas shift reaction (Ouyang and Besser 2005; Ouyang et al. 2005)

With this aim, catalytic Pt-loaded zeolite membranes were utilized as an effective device for CO selective oxidation in a single-stage membrane reactor operating in a continuous *flow-through* configuration at ca. 200 °C and a low feed molar ratio O₂/CO = 1 and 1.5 (Bernardo et al. 2008). This new model reactor design leads to improved and really interesting performance in terms of CO conversion and limited hydrogen consumption.

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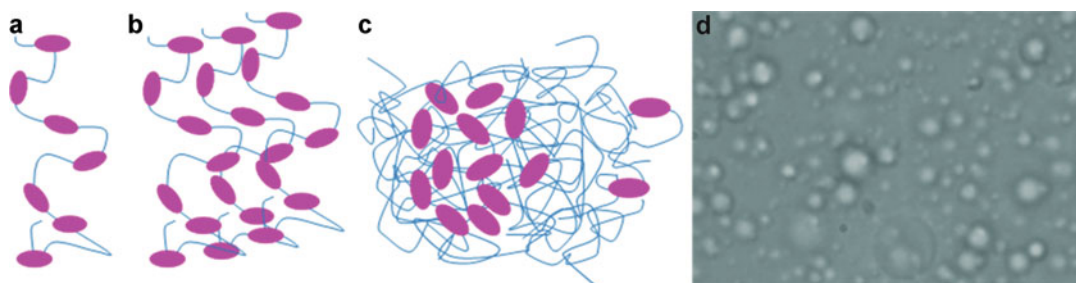
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Coacervation

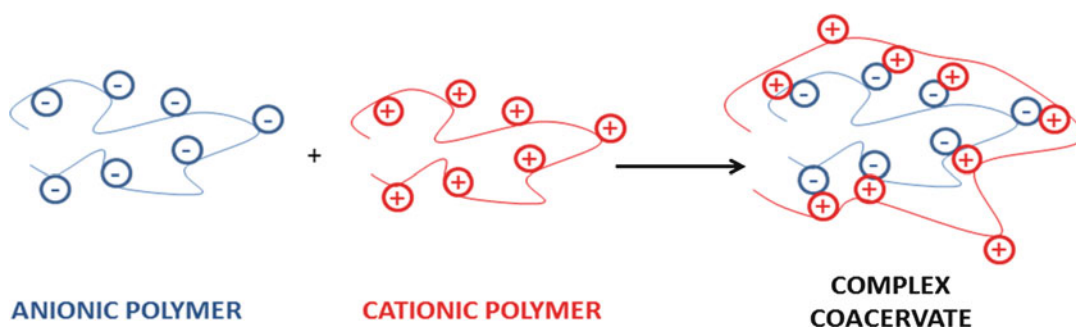
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Coacervation is a chemical method for producing polymer droplets in suspension based on the separation of two liquid phases into one concentrated colloidal phase, being the coacervate, and another highly dilute colloidal phase (Fig. 1). The phase



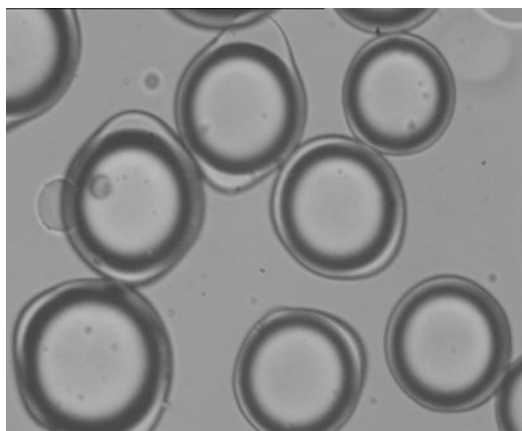
Coacervation, Fig. 1 Coacervate formation. (a) Intrapolymers complex, (b) soluble aggregate of intrapolymers complexes, (c) coacervate with dense and dilute domains, (d) coacervates picture



Coacervation, Fig. 2 Complex coacervate gels formed by mixing a polyanion polymer with a polycation polymer

separation of a single polyelectrolyte or a mixture of polyelectrolytes from a solution and deposition of the agglomerated colloidal particles (i.e., the matrix material) on an immiscible active core results in the formation of a simple coacervate or a complex coacervate, respectively (De Kruijff et al. 2004).

Phase separation in simple coacervation is brought about by addition of a salt, pH, or temperature change in the polymeric solution (such as alginate and calcium) while in complex coacervation is brought about by anion–cation interactions (such as gelatine and gum Arabic or chitosan and alginate). Complex coacervate gels can be formed by mixing of a polyanion with a polycation (Fig. 2). The underlying principle of this method is that polymers with opposite charges stick together and form soluble and insoluble complexes depending on the concentration and pH of the respective solutions. One such example is coacervating proteins with polysaccharides (Schmitt and Turgeon 2011).



Coacervation, Fig. 3 Microscopic view of the microcapsules obtained by complex coacervation

Proteins below its isoelectric point are positively charged and likely to associate with anionic hydrocolloids and form polyion complex hydrogel (complex coacervate).

Coacervation uses the principle of difference in ionic forces to cause the polymer(s) to form droplets and drop out of solution. A key to this is knowledge of the isoelectric point (PI) of the polymers and adjusting the formulation accordingly. Electrostatic effects and other weak energy interactions, especially hydrogen bonding, play a very important role during complex formation/coacervation between proteins and polysaccharides. Hydrophobic interactions can also make a significant contribution to formation of complexes and coacervates between oppositely charged biopolymers. Several physicochemical parameters influencing the overall and local charge of the protein and the polysaccharide play an important role in the control of the phenomenon such as pH, ionic strength, protein to polysaccharide ratio, and total biopolymer concentration. Some other parameters such as the biopolymer molecular weight and flexibility, the charge density, the stirring, the pressure, or the temperature have been shown to also influence complex formation.

Complex coacervation between oppositely charged proteins and polysaccharides is a well-known oil encapsulation technology (Fig. 3).

Typical steps of encapsulation by complex coacervation generally involve:

1. Emulsification (formation of the core) of a generally hydrophobic material in a solution comprising hydrocolloids
2. Coacervation (formation of the shell) implying the formation of a coacervate phase
3. Wall hardening (usually achieved by cross-linking the hydrocolloid forming the wall)

The step of wall formation is generally driven by the surface tension difference between the coacervate phase, the water, and the hydrophobic material. In most industrial coacervation processes, one of the hydrocolloids used in coacervation processes is selected from gellable proteins. These are easier to use and less prone to aggregation after the formation of the wall when the temperature is below the gelling temperature, if

compared to non-gellable hydrocolloids. Gelification, in turn, is generally brought about by lowering the temperature of the reaction mixture below the gelling point of the gellable hydrocolloid. The emulsification step can be carried out by homogenizing the oil with an aqueous sol of one colloid and mixing the emulsion with an aqueous sol of another colloid, or the two sols may be made and mixed and the oil emulsified therein. Complex coacervation occurred by lowering the pH until a pH is low enough to enough opposite electrical charges and form polymer complex. The coacervate phase is fluid and distributes over the oil surface forming the shell. The wall hardening renders the process irreversible and making the resulting microcapsules insoluble in water, resistant to mechanical stress and to heat exposure.

Cross-References

- [Membrane Emulsification in Phase Separation for Microcapsule Preparation](#)

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Coagulation Bath

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Phase Separation (PS) or Phase Inversion (PI) is among the principal techniques for membrane preparation. The membrane matrix and the

membrane pores are formed, respectively, from the polymer-rich and the polymer-lean phases originated by the phase separation of an initially homogeneous polymeric dope. Immersion of a cast (or spun) polymeric dope in a coagulation bath is normally used in nonsolvent (or diffusion)-induced phase separation (NIPS or DIPS), also called immersion precipitation (IP), to achieve such separation, often referred to as demixing or precipitation as well. Upon immersion in the coagulation bath, the initial composition of the dope changes as the solvent diffuses in the bath and is gradually replaced by the nonsolvent. Polymer precipitation due to solvent/nonsolvent (S/NS) exchange is exploited both in flat sheet and hollow fiber preparation via NIPS. However, for flat sheet membranes, the cast polymer film is immersed in the coagulation bath and phase inversion starts at the top surface of the film. Regarding hollow fibers, prepared via wet or dry/wet spinning, phase inversion takes place both at the inner and at the outer surfaces. While the term “coagulation bath” is normally used when referring to the media for the coagulation of the outer surface, the inner coagulant is often referred as bore fluid. In any case, the solvent/nonsolvent exchange is at the basis of the membrane preparation mechanism via immersion precipitation. Phase separation will occur only when the system composition, in terms of polymer/solvent/nonsolvent (P/S/NS) concentrations, reaches the miscibility gap, surrounded by the spinodal curve in the ternary phase diagram (at a selected temperature). Membrane morphology will be strongly affected by the coagulation bath composition and temperature, since they both influence the solvent/nonsolvent exchange rate and the polymer precipitation. In particular, the exchange rate depends on the mutual affinity between the solvent contained in the dope and the nonsolvent in the bath as well as on temperature. On the other hand, diverse nonsolvents usually display different coagulation power; polymer precipitation is affected by the nonsolvent nature and, obviously, by temperature. The mutual affinities between S/NS and P/NS are

often described in terms of Hildebrand's solubility parameters (δ). In general, it is known that the closer the values of the solubility parameters of two species, the higher the affinity between the two. Therefore, the difference between the S and the NS solubility parameters (δ_{S-NS}) can be used as a reference to estimate the S/NS exchange rate during coagulation: it will be faster if they have high mutual affinity, indicated by a small δ_{S-NS} . Furthermore, the difference between the P and NS parameters (δ_{P-NS}) can be used to infer about the coagulation power of a nonsolvent: strong, or harsh, coagulants are characterized by a higher δ_{P-NS} , while soft, or gentle, nonsolvents usually display a smaller δ_{P-NS} . The Hildebrand solubility parameter can be calculated, according to the Hansen's theory (Hansen 1967), as the square root of the sum of the squares of three components: δ_d , representing the energy from dispersion bonds; δ_p , the energy from dipolar intermolecular forces; and δ_h , the energy from hydrogen bonds between molecules. The strength of different NS can be also evaluated and, eventually, compared, by looking at the position of the binodal curve in the ternary phase diagram. In general, the curve moves towards higher NS percentages when using a softer coagulant. On the contrary, the binodal curve moves closer to the P-S axis, indicating less NS tolerance, when using a strong coagulant. The temperature of the coagulation bath will influence the interdiffusion rate between solvent and nonsolvent, which will be faster at higher temperatures. Polymer solubility in the S/NS mixture at any time during phase inversion depends on temperature, which affects the miscibility gap boundary position in the ternary phase diagram; this will mostly depend on the initial temperature of the casting solution but is affected by the coagulation bath temperature as well. Another factor that is known to affect the S/NS exchange rate is the molecular weight, since bigger size normally hinders diffusion. Solvent diffusion in the coagulation bath can be delayed by acting on the concentration gradient, i.e., by adding some solvent in the bath composition; this will also reduce the difference between the solubility parameters

of the polymer and the coagulant, which is not pure nonsolvent. The proper choice of the coagulation conditions allows to tailor membrane morphology. In general, it is known that membranes with open and porous structures can be obtained by fast demixing, while delayed demixing often results in the formation of a dense skin, with sponge-like or closed-cell morphology in the sublayer. Furthermore, fast demixing is one of the factors inducing macrovoids formation. For instance, when the as-cast polymer film is immersed in the coagulation bath, the polymer precipitation in the top layer will be faster with a strong coagulant, resulting in a porous skin; on the contrary, delayed demixing may result in the formation of a dense skin. However, the S/NS exchange can be properly delayed, by introducing some solvent in the coagulation bath or by using a soft coagulant, as a viable strategy to reduce macrovoids formation; in fact, it is accepted that the nonsolvent influx is responsible for voids growth during membrane formation.

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Coagulation Medium

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Synonyms

Coagulation medium (also known as nonsolvent bath, coagulation bath, phase-inversion medium, precipitating medium)

Definition

It is a liquid bath providing the precipitation of an extruded or cast polymer solution with the resulting formation of a solid membrane matrix.

Coagulation medium is responsible for the phase inversion process, and most of the time, it is represented by water. Some organic solvents (such as ethanol or isopropanol) can be also used to induce polymer precipitation, and even vapors and supercritical fluids can be considered as coagulation media for the phase inversion process.

In non-solvent-induced phase separation (NIPS), the polymer solution is cast upon a support and subsequently immersed into a coagulation bath (generally water) where polymer precipitation occurs. The choice of the appropriate coagulation medium represents a significant aspect in membrane preparation. The miscibility between solvent (in which the polymer is dissolved) and non-solvent can affect, in fact, the final structure of the membrane. The solvent contained in the cast film exchanges with the non-solvent contained in the coagulation medium inducing polymer precipitation.

Variable amounts of solvents can be also added to the coagulation medium giving two contrary effects:

Slow down the phase separation process leading to the formation of membranes with a less porous structure.

Decreasing polymer concentration at film interface leading to a membrane with a more open structure (Drioli and Giorno 2009).

Final membrane structure will, thus, depend on the miscibility between the two liquids and, therefore, on the mutual interactions established between them.

Even the temperature of the coagulation medium, used to precipitate the casting solution,

plays an important role. Generally low temperatures lead to the formation of membranes with a more dense structure (delay demixing) that find application in nanofiltration, gas separation, or reverse osmosis.

In vapor-induced phase separation (VIPS), the coagulation medium is represented by a non-solvent in a vapor phase. The vapor is generally water, and the precipitation occurs due to the affinity of the solvent (contained in the polymeric solution) for vapor (contained in the surrounding environment). VIPS technique leads to the formation of membranes with a porous structure usually applied in microfiltration. Relative humidity, temperature, and exposure time are the main variables affecting membrane morphology.

Other possibilities are supercritical fluids such as supercritical CO₂ that can be used as coagulation medium. Supercritical CO₂ can be used, in fact, as environmental friendly non-solvent leading to the formation of asymmetric membranes with the advantage of avoiding the collapse of membrane structure due to absence of a liquid–liquid or a liquid–vapor interface (Reverchon and Cardea 2004).

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Coagulation Medium (also Known as Nonsolvent Bath, Coagulation Bath, Phase-Inversion Medium, Precipitating Medium)

► Coagulation Medium

Cobalt Removal and Recovery by Supported Liquid Membranes

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Synonyms

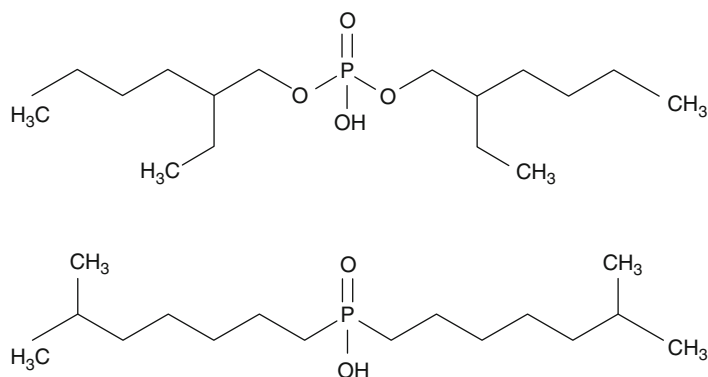
Co (II) ions separation by supported liquid membranes

Naturally found in some minerals as cobaltite, erythrite, or smaltite, cobalt is an element with different industrial applications, mainly in, i.e., electroplating and magnets or, as alloying element, for the fabrication of engines with high resistance to temperature.

Some cobalt salts have the ability of giving blue color, and, then, they have been extensively used as pigment for ceramics, glass, inks, etc.

Supported liquid membranes have been used as a tool for the recovery and removal of cobalt from different waste aqueous solutions. Typically, these solutions contain a mixture of metals that may complicate the selective separation of cobalt. Thus, in many cases, separation of cobalt by supported liquid membranes has to be performed in the presence of metals such as copper, cadmium, chromium, and specially nickel, which exhibits similar properties than cobalt. For a good and selective separation of cobalt ions from the rest of metallic element separation, it is essential to control the chemical conditions of the membrane separation process, mainly the correct selection of the organic carrier and the acidity of the aqueous source phase.

The mechanism of the separation process of cobalt by supported liquid membranes is based on the complexation and de-complexation reactions of cobalt ions present in the aqueous solution, with an extractant agent present in the organic liquid membrane. Although many organic reagents have been studied and applied at laboratory scale, the best



Cobalt Removal and Recovery by Supported Liquid Membranes, Fig. 1 Chemical structure of bis(2-ethylhexyl) hydrogen phosphate (1) and bis(2,4,4-trimethylpentyl) phosphinic acid (2)

results have been obtained when using organophosphorus acidic compounds, such as bis(2-ethylhexyl) hydrogen phosphate (1) or bis(2,4,4-trimethylpentyl) phosphinic acid (2) (Fig. 1).

Cobalt Removal and Recovery with Strip Dispersion

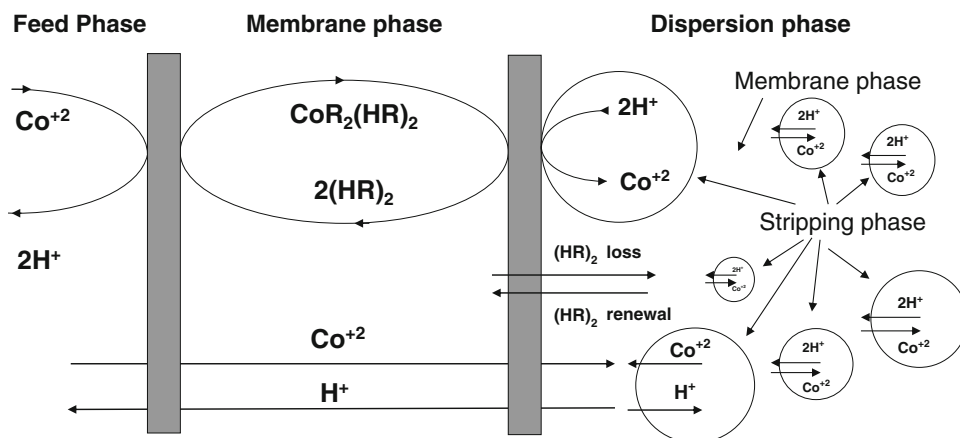
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The commercial success of supported liquid membrane has been seen to be limited due to the lack of long-term stability. Six mechanisms have been identified for supported liquid membrane instability (Kemperman et al. 1998). The two considered most important are emulsification of the liquid membrane phase and osmotic pressure difference over the membrane. In order to increase the stability of a supported liquid membrane (increasing simultaneously the efficiency of the separation process) by preventing the loss of the liquid membrane process, the use of the supported liquid membrane with strip dispersion has been described. This technique, first described by Ho (2001a), incorporates concepts of supported liquid membranes and of emulsion liquid membranes. It is also known as pseudoemulsion-based hollow-fiber strip

dispersion (PEHFSD), dispersion supported liquid membrane (DSLML), or emulsion pertraction (EP) due to the different configurations that have been used, mainly flat-sheet and hollow-fiber supported liquid membranes configurations. It has been applied to the removal and recovery of different organic species (organic acids, phenols, antibiotics, and alkaloids) and different metals (Co(II), Cr(VI), Cr(III), Cu(II), Au(III), etc.). Figure 1 shows a schematic representation of the technique.

As shown in this figure, the aqueous product phase, containing the stripping agent, is dispersed in the membrane organic phase, containing the carrier, and the water in oil dispersion formed is added (flat-sheet configuration) or is passed (hollow-fiber configuration) onto one side of the membrane support. The organic phase of the dispersion becomes imbedded in the pores of the microporous hydrophobic support of the flat or hollow-fiber configuration, forming a stable SLM. The constant supply of organic membrane solution into the pores of the membrane support ensures stable and continuous operation. The aqueous feed solution is added or passed on the other side of the membrane support, and the target specie is extracted into the organic solution by the selective carrier and then stripped by the aqueous strip solution (Fig. 1). For final recovery of the target specie, the mixer is turned off or a settler is used for the loaded strip dispersion, and the dispersion quickly separates. Supported liquid membranes with strip dispersion processes offer



Cobalt Removal and Recovery with Strip Dispersion, Fig. 1 Schematic representation of the carrier mediate counter-transport of cobalt (II) through supported liquid

membranes with strip dispersion using an organophosphorus acid as carrier

several advantages compared with other liquid membrane configurations, including the following (Klaassen et al. 2005): no emulsion formation in the water phase, flexible process parameters, phase separation is not necessary, compact modular equipment, low energy consumption, and large specific surface areas due to hollow-fiber contactors. This technique has been used for cobalt removal and recovery (Ho 2001b; Alguacil et al. 2011). Ho described several experiments using polypropylene as polymeric microporous support, in both flat-sheet and hollow-fiber configurations, di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) as carrier, Isopar L and dodecanol as organic diluent, and sulfuric acid as stripping agent. Alguacil et al. removed cobalt (II) from acidic sulfate solutions by using polypropylene as polymeric microporous support in hollow-fiber configuration, di(2-ethylhexyl) phosphoric acid (DP-8R) as carrier, Exxsol D100 as organic diluent, and sulfuric acid as stripping agent.

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Cold Plasma

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Cross-References

- [Emulsion Liquid Membrane \(ELM\)](#)
- [Hollow Fiber](#)

Plasma can be defined as a partially ionized gas which contains approximately equal numbers of positive and negative particles (Chapman 1980;

Chen 1974; Grill 1994; Thornton and Greene 1994; d'Agostino 1990; Milella 2008).

Plasmas can be roughly classified into hot plasmas (also defined as near-equilibrium plasmas) and cold plasmas (or nonequilibrium plasmas). Hot plasmas are characterized by very high temperatures of electrons and heavy particles (atoms, molecules, or ions) and they are almost fully ionized. In cold plasmas, instead, the electron temperature is relatively high (1–10 eV), while the translational energy of heavy particles remains very low, with temperature close to the room one and the ionization degree is typically low (around 10^{-4} – 10^{-6}). When an electric field is applied to a gas, energy is transferred more efficiently to the free electrons naturally present in the gas than to the ions. The accelerated electrons, then, transfer the energy to heavier particles through elastic and inelastic collisions. At low pressure the collision frequency is very low; moreover, because of the large mass difference between electrons and heavy particles, the transfer of kinetic energy is inefficient. Hence, in this nonequilibrium state, the gas temperature cannot increase, while electrons gain enough kinetic energy to promote excitation, ionization, fragmentation, and formation of reactive species by inelastic collisions with heavy particles. In this scenario, energetic electrons can produce high temperature chemistry in a gas at low temperature, and this allows the treatment of thermally sensitive materials like polymers.

Since electrons are much faster than other particles, every surface immersed in the plasma immediately develops a negative charge which accelerates ions. As a matter of fact, the plasma potential is always the most positive one.

A low-pressure cold plasma apparatus typically consists of a vacuum chamber, a pumping unit, a gas feeding system and gas controllers, pressure gauge, a power supply, and a power transfer device. Electrodes can be driven both by AC and by DC power supply. AC discharges, commonly run in the radiofrequency (RF) and microwave (MW) range, are more stable and suitable for insulators (e.g., ceramic and polymers) processing. In case of RF glow discharges, the operating frequency is generally 13.56 MHz in order to avoid interferences with

communications. At this frequency, only electrons can follow the instantaneous variations of the applied electric field, while ions are driven by an average potential.

At the steady state, the total ion and electron charge flow to a given electrode during an RF cycle must balance to zero and a self-bias that is negative with respect to the plasma potential develops. If the surface is electrically isolated, the potential at the steady state is named floating potential and it is also negative with respect to the plasma potential. As a consequence, each surface immersed in a plasma will be bombarded by ions.

It should be also highlighted that cold plasmas can be also ignited at atmospheric pressure, and since the late 1980s, an increasing interest has grown in the application of such plasmas (e.g., dielectric barrier discharge, corona, and atmospheric jet) to material processing (Kogelschatz 2003).

Cold plasmas can modify the surface of material by depositing thin films (plasma-enhanced chemical vapor deposition), by grafting specific chemical functionalities (plasma treatment), or by ablating materials (plasma etching).

Membranes can be processed by means of cold plasmas to activate the surface by introducing specific chemical groups such as hydroxyl, carboxyl, and amino moieties. This can be accomplished by feeding the plasma non-polymerizable gases/vapor such as O₂, H₂O, NH₃, and N₂/H₂. Alternatively, functionalized coatings can be deposited for the same purposes (e.g., acrylic acid or allylamine based). These treatments allow to tune surface properties of membranes, notably wettability and molecular adsorption, or to serve as anchor for specific biomolecules or catalysts (Favia et al. 2008; Fontananova et al. 2006; Roualdes et al. 2010).

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Complexation–Ultrafiltration Process for Heavy Metal Removal from Effluents

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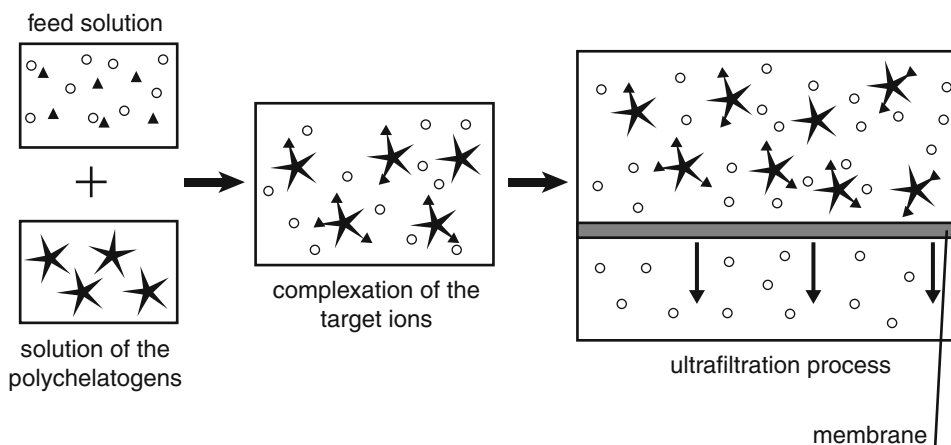
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Metal rejection in aqueous solution containing Ni (II), Cu(II), and Cr(III) ions was evaluated (Barakat and Schmidt 2010) using complexation–ultrafiltration. The filtration experiments were performed with ultrafiltration membrane system, equipped with a polyethersulfone membrane (Figs. 1 and 2) with a 10,000 Da cutoff. The pressure was fixed at 1 bar with a permeate flow rate of 7.5 L/h, while CMC was used as a complexing agent. The process is pH dependent, and the metal rejection was more efficient at neutral and alkaline conditions than at acidic one. Metal rejection efficiency values were 97.6 %, 99.5 %, and

Combined Fouling Index (CFI)

► Fouling Index



Complexation–Ultrafiltration Process for Heavy Metal Removal from Effluents, Fig. 1 Principles of complexation–ultrafiltration process (Rether and Schuster (2003))



Complexation–Ultrafiltration Process for Heavy Metal Removal from Effluents, Fig. 2 Complexation–ultrafiltration system

99.1 % for Cu(II), Cr(III), and Ni(II) ions, respectively, at pH 7. The membrane had worked efficiently on a wide range of concentration up to 100 mg/l for both of Cu (II) and Cr (III) ions, while the Ni(II) ion rejection efficiency decreased to 57 %. The process is characterized by low energy requirements involved in the ultrafiltration, the very fast reaction kinetics, and the high selectivity for the metal ion separation.

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Composite Membrane with Inorganic Fillers: Electrolyser Application

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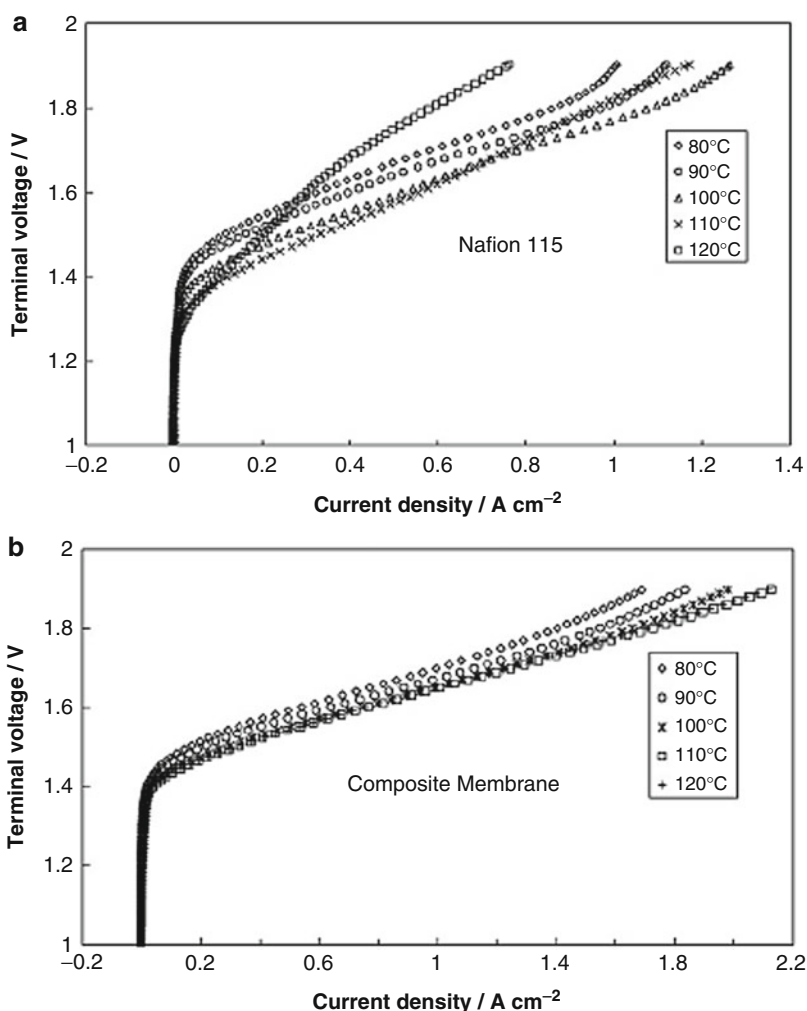
Composite Membrane with Inorganic Fillers: Electrolyzer Application

Composite recast Nafion[®] membranes containing inorganic fillers have been primarily employed in fuel cells for high-temperature operation (Aricò et al. 1998) and self-humidification purposes (Watanabe et al. 1996). Composite membrane with inorganic fillers for electrolyzer application has been developed in order to extend the operating temperature range of polymer electrolyte membrane (PEM) electrolyzer and to reduce gas crossover effects (Antonucci et al. 2008).

Generally, Nafion[®] membrane is used as conducting polymer electrolyte in PEM electrolyzer systems. An increase of the operation temperature of an electrolyzer should enhance the oxygen evolution reaction rate that is the rate-determining step of this process allowing to obtain high current and high conversion efficiency. However, commercial Nafion membranes loose conductivity at temperature above 100 °C due to membrane dehydration. Perfluorosulfonic acid (PFSA) composite membranes containing hygroscopic ceramic oxide

fillers that require water for proton conduction appear suitable for this application especially in the light of the high operating pressure of PEM electrolyzers (up to 100 bars) that allows to maintain a good fraction of liquid water even at temperatures above 100 °C. The inorganic fillers enhance the water retention inside the composite membrane allowing to operate properly at high temperatures. A composite Nafion–SiO₂ membrane for SPE electrolyzers has shown promising properties for high-temperature operation allowing to achieve significantly higher

Composite Membrane with Inorganic Fillers: Electrolyser Application, Fig. 1 Polarization measurements for a PEM water electrolysis cell based on conventional Nafion 115 and composite PFSA–SiO₂ membrane at various temperature and 3.0 bar abs pressure



performances with respect to a bare commercial Nafion. This effect is mainly due to a significantly better water retention than the bare perfluorosulfonic membrane and lower gas crossover as a result by the increased tortuosity effect produced by the inorganic filler inside the membrane. The performance of the electrolyzer based on Nafion-SiO₂ membrane increased as a function of the temperature up to 120 °C and pressure. A maximum current density of about 2.1 A cm⁻² versus 0.7 A cm⁻² at 1.9 V, 120 °C, and 3 bar abs was recorded for the composite membrane compared to Nafion 115 (Fig. 1). An increase of electrical efficiency was recorded at low current densities for the high-temperature SPE electrolyzer compared to conventional membrane-based devices (Antonucci et al. 2008).

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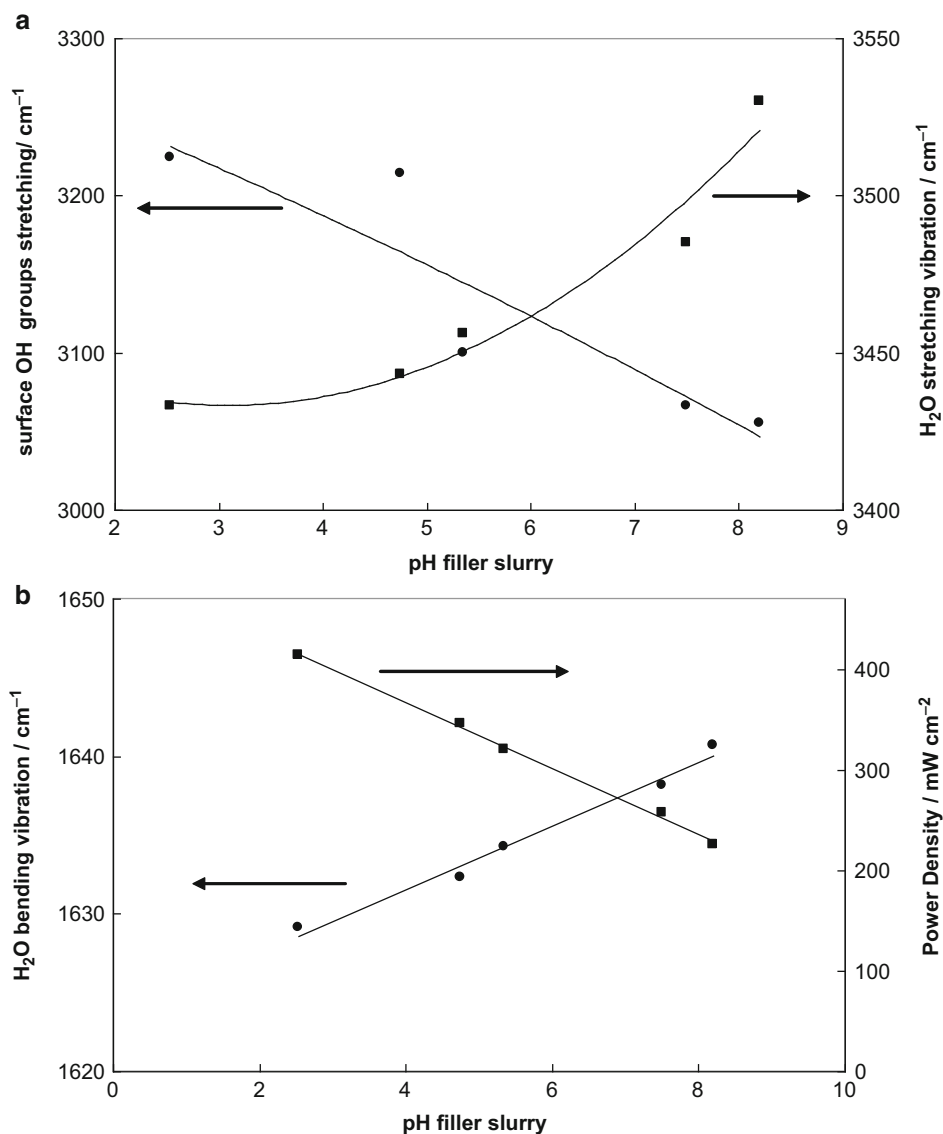
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Composite Membrane with Inorganic Fillers: Fuel Cell Application

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Composite recast Nafion[®] membranes containing inorganic fillers have been employed in high-temperature (~150 °C) direct alcohol (Aricò et al. 1998) and H₂-air fuel cells (Watanabe et al. 1996). These composite membranes were

originally developed for reduced humidification operation in polymer electrolyte fuel cells (Watanabe et al. 1996) due to the enhanced water retention inside the membrane by the effect of the inorganic filler (Aricò et al. 1998). A further advantage of composite membranes relies in the barrier effect given by the inorganic filler for methanol cross over (Ren et al. 1996) which is of particular relevance at high temperature. It is well known that the physical adsorption of water by materials such as silica (one of the most used inorganic fillers) is mainly determined by their surface properties; similar considerations can be made for other hygroscopic inorganic oxides such as alumina. Functional groups on the surface of these oxides are believed to act as water coordination centers (Aricò et al. 2003). FTIR analysis of various silica materials suggests that oxygen surface functionalities play a prevailing role in the adsorption of water. The surface characteristics of an inorganic oxide can be modified by thermal treatments in inert or oxidizing atmosphere through reactions with strong inorganic acids (Aricò et al. 2003). Most of the works on composite membranes have addressed the technical aspects related to the use of these materials as electrolytes in high-temperature fuel cells. Accordingly, performance, conductivity, and stability characteristics have been investigated in-depth. Parallel work has been concerned with the investigation of relevant filler properties for application in composite membranes such as surface area analysis, surface chemistry studies, and surface acid-base investigations of the fillers. The conductivity of perfluorosulfonic acid (PFSA) composite membranes and fuel cell power density at high temperature have been found to be related to the characteristics of the water adsorbed on the filler particles. Inorganic fillers characterized by acidic properties undergo a strong interaction with water and enhance the DMFC performance at high temperature. Appropriate selection of the surface properties for the inorganic fillers thus allows to enhance proton conductivity and fuel cell performance and extends the operating temperature range of composite membranes (Aricò et al. 2003; Fig. 1).



Composite Membrane with Inorganic Fillers: Fuel Cell Application, Fig. 1 Relationships between water adsorption characteristics of inorganic fillers and

corresponding performance of a composite membrane-based direct methanol fuel cell at 145 °C

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Computational Fluid Dynamics (CFD) and Membranes

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The increasing number of CFD membrane studies is clearly related to the recent developments in computer power and to the use of finer grid meshes in the vicinity of the membrane. Two approaches have been particularly considered: the comprehension of the hydrodynamics and of the mass transfer.

The hydrodynamics allows the increase of the shear stress near the wall or the transmembrane pressure thus allowing the enhancement of permeate flux and the membrane processes. CFD allows determining the hydrodynamics, i.e., the pressure and velocity fields, taking into account the geometry of the module and the membranes, the membrane permeability and compactness, as well as the operating entry values such as filtration or backwash pressures, filtration mode, and gravity. For example, it is possible to determine the pressure and velocity fields in (i) a hollow fiber module containing more than 40,000 fibers (small diameter ($d_i = 0.93$ mm) and large flow rate ($50 \text{ m}^3 \cdot \text{h}^{-1}$) or in (ii) ceramic multichannel membranes or module to obtain information about the wall shear stress distribution at the surface of the membrane. The study of hydrodynamics reveals the optimum operating conditions and the most suitable geometry characteristics to determine a compromise between membrane area, channel (geometry and number), and energy consumption to optimize membrane processes. A large number of studies relate to the diphasic flows, to the turbulence promoters, and to the geometries of membranes capable of generating secondary flows. Usually a good agreement is obtained between CFD and experimental data obtained for the transfer of solvent. Some recent studies consider turbulent flows and the significant number of

turbulence models in numerical simulations, and their comparison with experimental results in the case of membrane processes is not excellent, which limits the use of CFD in turbulent regime.

Fouling remains a major problem in membrane processes: this phenomenon limits the process efficiency and is difficult to predict and anticipate. These difficulties are linked to the complexity of this phenomenon which implies different interdependent mechanisms occurring at pore scale. The relative importance of each fouling mechanism has been determined according to the particle size, the pore size, and the surface density of pores. By CFD progress it is now possible (a) to pursue the description of the different fouling mechanisms by integrating the complexity of the real membrane structure in the numerical simulation and (b) to simulate different kinds of experimental deposit structure. The limitation is the membrane reconstruction technique limiting this description at the MF and UF membranes. The filtration in a cylindrical pore (i.e., microchannels) can be simulated for different sizes of particles or pores, tortuosities, and hydrodynamic conditions. For these CFD studies, the difficulties are to well describe particle/particle colloidal interactions and resuspension of particles after capture.

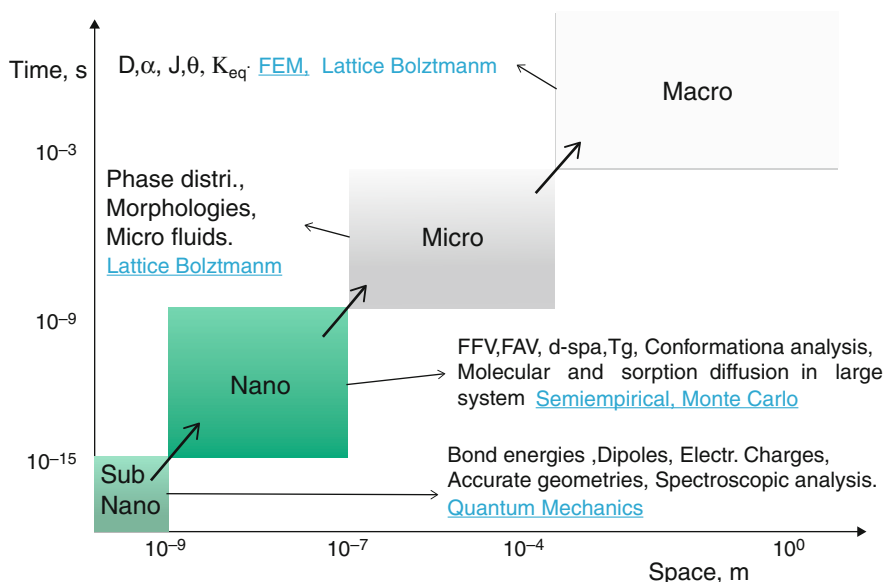
Thus, CFD is without any doubt an important tool for understanding mass transfer in membrane processes, and opportunities for the development of new membrane geometries are numerous.

Computer-Aided Methods and Tools

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Computational methods can be divided into approaches using adjustable or empirical parameters and those which do not use them. Concerning the first methods, several procedures have been developed for the optimization of the adjustable parameters. For example, design of experiments is



Computer-Aided Methods and Tools, Fig. 1 Computational methods and achievable properties

an approach defining the minimum number of experiments required to obtain the fitting parameters. Instead, in the *ab initio* methods, these quantities are obtained by direct experimental measurements or from other simulations carried out in smaller time-space scale (Steinhauser 2008), until the sub-nanometer scale is reached.

The choice of the computational approaches strictly depend on the properties to be studied. Figure 1 shows the various computational methods and properties that can be obtained.

Binding energies, molecular electrostatic properties must be evaluated by quantum mechanics (QM) approaches (Veszprémi and Fehér 1999). These generally require significant computational resources, although the development of parallel supercomputers and efficient algorithms have allowed to carry out QM calculations unthinkable few years ago. The quantities, obtained at QM level, can be used in subsequent molecular dynamics (MD), Monte Carlo (MC), or semiempirical calculations to describe properties related to a huge number of molecules and atoms, like polymers. MD methodologies are based on the simultaneous solution of Newton's equation of motion referred to the atoms of the physical system (Allen and Tildesley 2003). The potential energy surface (interaction potential), also called

force field (FF), used in the MD simulations is defined by QM or parameterized over measurements. The temperature, volume, pressure, and number of particles define the statistical ensemble in which the MD can be performed. The classic MC method is generally based on the von Neumann, Metropolis, and Ulam algorithm (Metropolis and Ulam 1949; Wood 1986). Later, the method has grown to the point where it leads to several methods all belonging to the MC family. In the grand canonical MC ensemble, the simulations are performed at chemical potential, volume, and temperature constant, whereas the number of molecules varies. The potential surface energy is always defined by means of a specific FF. Interesting MC approaches are based on the quantum MC methodology. The semiempirical methods use Hamiltonians to describe the system, but some contributions of these operators are obtained empirically (Clementi and Corongiu 1995). These approaches allow to evaluate the target properties more quickly than the QM methods. In Table 1, the illustrated computational methods are summarized with their advantages and disadvantages.

The information provided by smaller scales can be utilized in mesoscale calculations: coarse grain MD or Lattice Boltzmann (LB) (Swift

Computer-Aided Methods and Tools,
Table 1 Advantages and disadvantages of some computational methods

Method	Advantages	Disadvantages
Molecular mechanics and Monte Carlo dynamics	Systems of thousands of atoms, low computational costs	Experimental data or values from quantum mechanics, absence of bond breaking/forming. Noncovalent bonds are not well described, less general
Semiempirical	Less computational demand than quantum mechanics approaches, systems of hundreds of atoms	Experimental data or values from quantum mechanics, less general
Ab initio, density functional theory quantum mechanics	Do not depend on experimental data, useful for a broad range of molecules without available experimental data, general	Computationally very expensive Small systems

et al. 1996). In particular, LB is a powerful method for simulating fluid confined in microsystems, as may be precisely a membrane. This method allows to solve the Navier-Stokes equations in a simple way and with a notable reduction of computational time. LB allows an easy description of the interfaces and especially without the use of adjustable parameters as made by the conventional finite elements methods (FEM). Finally, the description of the properties of macrosystems can be carried out using methods based on classic mechanics or dynamics. The differential equations describing these physical systems are evaluated numerically by means of FEM or finite volume procedures (De Luca et al. 2014). There is a notable number of codes implemented for each method just described. These are divided into programs in which a single methodology is implemented or those in which several methods, radically different, can be found. Therefore, it is possible to find codes in which only QM (based on different theories) or MD are implemented

separately and others in which both the methodologies are present. Particular attention should be given to parallel algorithms since parallel supercomputers allow the use of huge number of processors (or computers interconnected by the net). These possibilities allow to perform complex calculations in short computational time.

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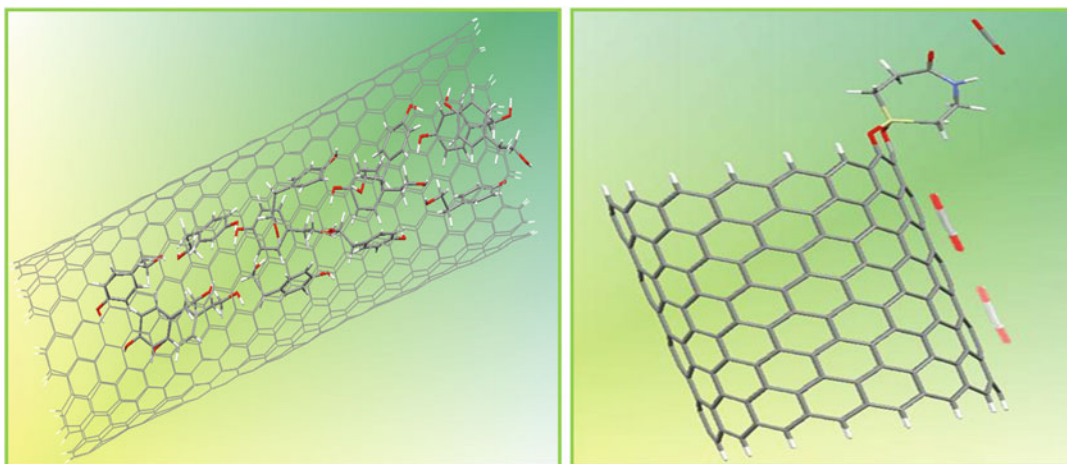
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Computer-Aided Models

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Models can be divided into mathematical and structural (chemical models), both connected to each other. Mathematical models and procedures can be numerical algorithms, in which each single step is simple arithmetic and logical relations, or they can be defined by analytical relationships, regardless of how they are evaluated. In either case, mathematical models and procedures are the result of some assumptions or approximations



Computer-Aided Models, Fig. 1 CNT structural models

based on structural or chemical models (Allen and Tildesley 2003; De Luca et al. 2006, 2008). For example, the description of a droplet formation during membrane emulsification by means of analytical force-balance relationships requires some approximations about the droplet shape and its evolution along the membrane membrane pore. Moreover, the shape of the membrane pores should be also modeled. Therefore, any mathematical model can be correlated with structural or chemical models. By using computational procedures, starting from quantum mechanical calculations, molecular dynamics (MD) or Monte Carlo (MC), in fact particular attention should be paid to the molecular (chemical) models. Molecular models are closely dependent on the target properties to be assessed as well as on the computational time required to get these properties. Computational time, in turn, depends on the level of theory used, that is, the mathematical approaches.

For example, at the moment, quantum mechanical methods are not applicable to optimize the geometry of macromolecules as polymers or systems containing thousands of atoms like biological systems. Molecular dynamics methodologies or coarse grain Monte Carlo can be used in these cases. However, molecular dynamics approaches cannot be used to study systems in which the breaking and formation of bonds or noncovalent bonds are decisive. Thus, in the latter case, the choice of a chemical model of macromolecules is

crucial. These structural models, also called analogues, inevitably lead to neglect some aspects; nevertheless in some cases these may be irrelevant if the choice of the analogues is done correctly. In fact, albeit molecular models certainly introduce approximations in the evaluation of the macromolecular or biological proprieties, some functions of these only depend on a limited part of the whole structures. Thus, chemical models can mimic very well the function of complex systems (Gademann et al. 2007; Zürcher et al. 2006; Saxer et al. 2010). Some examples, concerning models of carbon nanotubes (CNT), have been presented in Fig. 1. In summary, mathematical models, computational methods, and structural (chemical) models carefully tune as a function of the type of calculation which is required to be done. Huge literature exists about studies on any kind of chemical models (*periodic surfaces, slabs, or clusters*) and correlated computational procedures (*periodic calculations, embedded clusters, and quantum mechanics/molecular mechanics methods, etc.*).

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Concentration Polarization Coefficient (CPC)

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Concentration polarization coefficient (indicated in the literature as *PC* or *CPC*). The

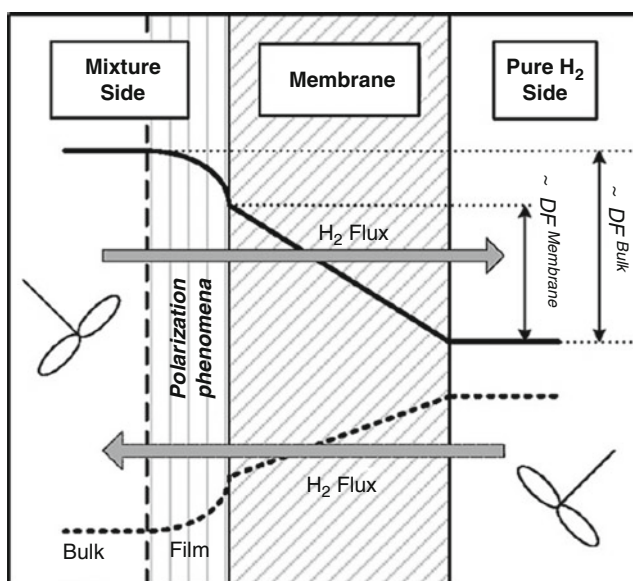
concentration polarization coefficient is a measure of the concentration polarization extent in a membrane-aided separation system. In general, the concentration polarization coefficient indicates the degree of permeation driving force lost with respect to the total driving force between the bulks of the fluid phase of feed and permeation side (Fig. 1).

In the open literature, it is possible to find several different definitions of *CPC* (see Table 1 for the most used), leading to different quantifications of this phenomenon. All definitions refer to a key species permeating through the membrane. In particular, for constant total pressure in feed and permeate side, the definitions of Wijmann et al. (1996), Yeom et al. (2002), and Zhao et al. (2008), who used a coefficient per each membrane side in order to take into account also the polarization in the downstream side, are in fact coincident. Based on these definitions, *CPC* tends to zero for increasing polarization, going toward the unity in the opposite situation (no polarization).

On the contrary, Wang et al. (2002) defined the *CPC* in such a way that it be close to the unity when concentration polarization is significant. A more useful definition is provided by Haraya et al. (1987) and Takaba and Nakao (2005), who considered a unique coefficient for accounting the polarization on both the membrane sides (Table 1).

Concentration Polarization Coefficient (CPC), Fig. 1

Schematic representation of the driving force (*DF*) drops along the permeation direction in case of hydrogen permeation through Pd-based membranes. The *solid* and *dashed* lines indicate the forward and backward permeation case, respectively. The profiles are expressed in terms of equivalent partial pressure (Adapted from Caravella et al. (2009))



Concentration Polarization Coefficient (CPC), Table 1 Most used definitions of concentration polarization coefficient in the literature

CPC definition	Range	References
$\frac{c_i^{\text{Film}}}{c_i^{\text{Bulk}}} \bigg _{\text{Feed}}$	(0, 1)	Wijmann et al. (1996) Yeom et al. (2002)
$\frac{x_i^{\text{Film}}}{x_i^{\text{Bulk}}} \bigg _{\text{Feed, Permeate}}$	(0, 1)	Zhao et al. (2008)
$1 - \frac{x_i^{\text{Film}}}{x_i^{\text{Bulk}}} \bigg _{\text{Feed}}$	(0, 1)	Wang et al. (2002)
$\frac{N_1}{N_1^0}$, for single-species permeation $\frac{N_1}{N_2}$, for multispecies permeation	(0, 1) (0, ∞)	Zhang et al. (2006)
$\frac{x_i^{\text{Film}}}{x_i^{\text{Bulk}}} \bigg _{\text{Feed}} - \frac{x_i^{\text{Bulk}}}{x_i^{\text{Bulk}}} \bigg _{\text{Permeate}}$	(0, 1)	Haraya et al. (1987) Takaba and Nakao (2005)
$\frac{\Delta \sqrt{p_{\text{H}_2, \text{Film}}}}{\Delta \sqrt{p_{\text{H}_2, \text{Bulk}}}} = 1 - \frac{\Delta \sqrt{p_{\text{H}_2, \text{Membrane}}}}{\Delta \sqrt{p_{\text{H}_2, \text{Bulk}}}}$	(0, 1)	Caravella et al. (2009)

c concentration, *x* molar fraction, *N_i* actual flux of the *i*th species, *N_i*⁰ flux of the *i*-th species without concentration polarization

In order to link the polarization effect to the selectivity of a membrane, Zhang et al. (2006) used the permeating fluxes in the *CPC* definition without specifying any explicit form of driving force.

In general, for *CPC* to provide an appropriate quantification of the driving force loss, it is advisable to define it using the driving force characteristic of the permeation mechanism that takes place. By doing this for hydrogen permeation through Pd-based membranes, Caravella et al. (2009) defined the *CPC* using the Sieverts characteristic driving force, as indicated in Table 1. In this case, the *CPC* is equal to zero in systems without polarization, tending to the unity for maximum polarization (external mass transfer controlling the overall permeation process).

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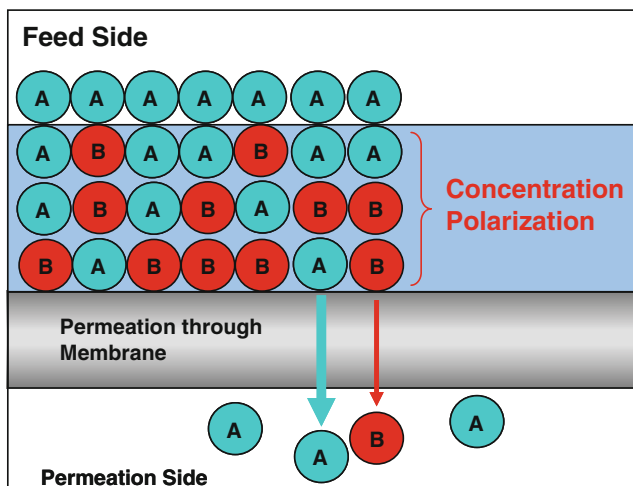
Concentration Polarization in Gas Separation

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In a separation process using membranes, *concentration polarization* (see also *bed-to-wall mass transfer limitations*) consists in decrease of the

Concentration Polarization in Gas Separation,

Fig. 1 Sketch of the concentration polarization phenomenon. The presence of the less-permeating species (b) generate a resistance to the flux of the more permeable species (a)



permeation driving force of more permeable species through the membrane because of the presence of less permeable species, which act as an additional resistance to permeating flux. The scheme reported in Fig. 1 provides the physical situation leading to concentration polarization. In particular, the species B is pushed toward the membrane surface by the effect of the flux of the species A. In these conditions, there is also a split in the respective concentration of the two species, which means that the concentration of the more permeable species A tends to be higher in the bulk of the feed fluid phase, while at the same time, the concentration of the species B tends to be higher in the proximity of the surface. From this point of view, it is possible to say that the concentration polarizes, analogously to what occurs in electrical polarization, where electric charges accumulate toward the respective electrodes.

In practice, concentration polarization occurs in every membrane-aided device and cannot be completely removed, but rather minimized. Furthermore, the higher the membrane selectivity (or separation factor), the higher the effect of concentration polarization, because the removal of the non-permeating species from membrane surface becomes more difficult.

Historically speaking, the first field where causes and effects of concentration polarization were analyzed in detail (since the beginning of the 1960s) was the liquid separation processes through membranes – such as ultrafiltration and

reverse osmosis. On the contrary, in the same period, concentration polarization had been considered negligible in gas separation, both because of the low the membrane performance in terms of permeation flux and because gases have diffusivity of four to five orders of magnitude higher than liquids (He et al. 1999).

However, the progresses obtained in the last decades in the field of membrane preparation for gas separation allowed increasing significantly the transmembrane flux of the key species to separate. The higher permeation flux causes the less-permeating species to concentrate (“polarize”) around the membrane surface, generating a phenomenon similar to the electrical polarization, from whose analogy concentration polarization takes its name.

In these conditions, the influence of the selective layer decreases with respect to the resistance of the external mass transfer can affect seriously the membrane performances up to become one of the slowest elementary steps of the overall permeation process (Caravella et al. 2009).

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Concentration Profile

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The concentration of a chemical species that is present in a certain volume of space V with a certain amount of mass is defined as the ratio between this amount of mass and the volume V . It can be expressed in terms of moles (i.e., molar concentration c_i [mol m⁻³], Eq. 1) or mass (mass concentration or mass density ρ_i [kg m⁻³], Eq. 2).

$$c_i = \frac{n_i}{V} \quad (1)$$

$$\rho_i = \frac{m_i}{V} \quad (2)$$

In general, a (nonconstant) concentration profile can be established because of the presence of sources/sinks (distributed and or concentrated) of momentum, mass, and/or energy in some locations within the physical domain considered.

In *membrane technology*, researchers are mostly interested in the evaluation of concentration profiles both through membrane and in membrane device, including the fluid phase in feed and permeate side. As for the former, the transmembrane flux J_i [mol s⁻¹ m⁻²] and, thus, the concentration profile of the i th species through membranes are promoted by a difference of its chemical potential μ_i [J mol⁻¹] between feed and permeate side (Eq. 3) (Wijmans and Baker 1995; Bachorczyk et al. 2003; Hara et al. 2012).

$$J_i = -L_i \frac{d\mu_i}{dy} = -c_i B_i \frac{d\mu_i}{dy} \quad (3)$$

In Eq. 3, L_i is a proportionality factor (not generally constant), B_i is the mobility (i.e., a measure of the aptitude of the i th species to pass through membrane), and y indicates the permeation direction (normal to membrane surface).

If the permeation driving force is mainly generated by partial concentration and pressure, the

permeating flux can be mathematically expressed as follows:

$$\frac{d\mu_i}{dy} = RT \frac{d\ln(\gamma_i x_i)}{dy} + \bar{v}_i \frac{dP}{dy} \quad (4)$$

where P [Pa] is the total pressure, γ_i is the activity coefficient linking the molar fraction x_i [mol mol⁻¹] to the activity a_i [–], and $\bar{v}_i$ [m³ mol⁻¹] is the partial molar volume. Based on the different permeation models to apply to different membrane types (dense or porous), different concentration profiles are established through the membrane.

The most common permeation models for dense and porous membranes are the solution-diffusion model and the pore-flow model. The former assumes that the pressure within a membrane is uniform and that the chemical potential gradient across the membrane is expressed only as a concentration gradient. The latter assumes that the concentrations of solvent and solute within a membrane are uniform and that the chemical potential gradient across the membrane is expressed only as a pressure gradient.

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Constant-Volume Diafiltration

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Constant-volume diafiltration (also called constant-volume dilution mode) is a batch

diafiltration process for separating microsolute from macrosolutes, in which the volume of the process liquor is kept constant during filtration by continuously adding a diluant into the feed tank at a rate equal to the permeation rate. The schematic representation of its configuration is shown in Fig. 1. The constant tank volume can be maintained by the use of a ball float valve or by means of liquid level controller (Beaton and Klinkowski 1983). As filtration progresses, the concentration of membrane-permeating microsolute in the feed tank continuously decreases, while that of the macrosolutes remains ideally unchanged (or close to constant in case of incomplete rejection).

Note that some literature sources misleadingly refer to “constant-volume diafiltration” as “continuous diafiltration.” Although the addition of diluant is performed in a continuous manner, constant-volume diafiltration should not be considered as a continuous process. It is a true batch process. It is advised, however, to use the term “constant-volume dilution mode” which is less common in the literature. The term “dilution mode” reveals that this technique is actually an operational mode of a membrane filtration process in which the process liquor is diluted with pure solvent.

Depending on the technological goal, either the permeate or the retentate represents the phase of primary economic importance. Thus, the product of the operation is either formed in the feed tank as a purified mixture of macrosolutes or collected in the permeate tank where the microsolute is accumulated. Both treatments pose a dynamic modeling problem. A mass balance on component

i in the feed tank gives the following initial value problem for its concentration $c_{f,i}(t)$:

$$\begin{cases} \frac{dc_{f,i}}{dt}(t) = \frac{c_{f,i}(t)q(t)[R_i(t) - 1]}{V_f} \\ [3 \text{ mm}]c_{f,i}(0) = c_{f,i}^0 \end{cases}$$

where $q(t)$ and $R_i(t)$ are the permeate flow and the solute rejection that are subject to change during operation. The constants V_f and $c_{f,i}^0$ denote the volume of the feed tank and the initial feed concentration of component i . The equation describes the evolution in time of the feed concentration $c_{f,i}(t)$ assuming that the diluant consists of no component i and the feed tank is well mixed.

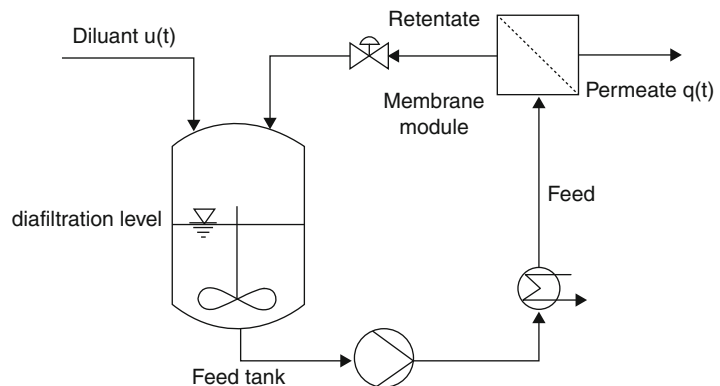
In many applications, the flux and the rejections are concentration-(inter)dependent quantities (Kovács et al. 2009) and may vary with operating conditions such as temperature, applied pressure, and hydrodynamics. In such cases, no closed form solution of the set of resulting complex differential algebraic equations exists; thus, numerical techniques are required to solve the model equations. Under the simple assumptions of constant permeate flow and rejections, however, the problem can be reduced to the following algebraic expression:

$$\ln\left(\frac{c_{f,i}(t)}{c_{f,i}(0)}\right) = D(R_i - 1)\% \quad \text{for } i = 1, 2, N$$

where D is the diafiltration factor (also called diavolume) that is defined as the ratio of applied volume of diluant to feed volume. For applications where the objective is to reduce the microsolite concentration by a fixed amount, the

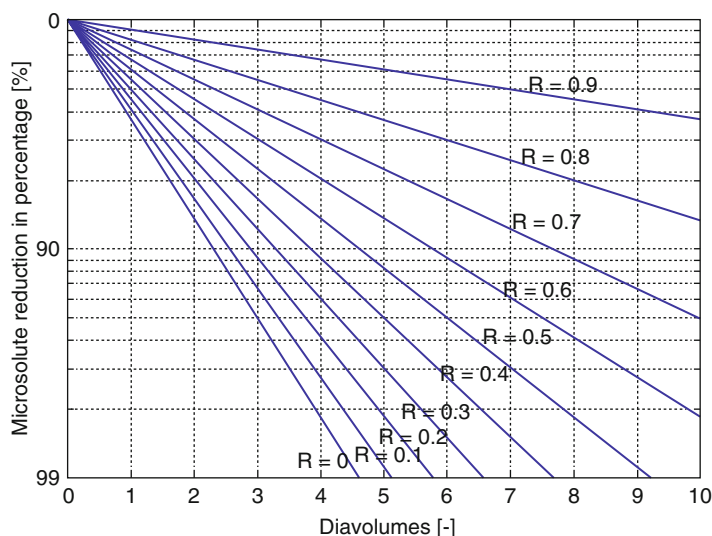
Constant-Volume Diafiltration,

Fig. 1 Schematic representation of constant-volume diafiltration settings



Constant-Volume Diafiltration,

Fig. 2 Dependence of microsolute removal on applied diavolumes in constant-volume diafiltration



necessary diavolumes can be determined based on Eq.2 as illustrated in Fig. 2.

In practice, constant-volume dilution mode is frequently preceded and/or followed by batch concentration operational steps in order to reduce the initial feed volume to a desired level and, thus, to concentrate the macrosolutes (for further details, see entry on “traditional diafiltration”).

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Contactor-Type Catalytic Membrane Reactor

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Synonyms

Catalytic diffuser; Pore-through-flow catalytic membrane

The term “catalytic membrane contactor” refers to a device in which a membrane containing a catalytically active phase is used to provide the reaction zone for conversion of one or more reactants from one or more fluid phases (Dittmeyer and Caro 2008). The membrane not always has a separation function, it provides the surface-rich reaction zone for a gas-liquid, but also for a gas-gas and a liquid-liquid reaction. Applications of membranes with built-in catalysts for gas-liquid reactions have been also reviewed in Dittmeyer et al. (2004).

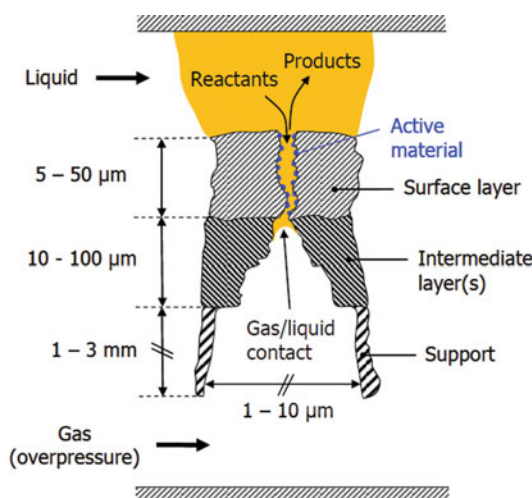
The catalytic diffuser concept can be utilized for solid-catalyzed gas/liquid reactions in various ways. If the membrane is not wetted, the operation principle is similar to that of a membrane contactor. The gas is on the support side, and the liquid is pumped through the shell side. The gaseous reactants enter the liquid phase at the gas/liquid contact plane which is established at the pore mouth towards the external membrane surface. The catalyst is deposited on this surface and gets in contact with the reactants. On the contrary, if the membrane is wetted the gas and not the liquid is at overpressure as described in Dittmeyer and Caro (2008).

Gas-liquid contactors without catalytic function can be used in gas adsorption. Examples are carbon dioxide removal from gas mixtures using monoethanolamine (Simons et al. 2009) or ionic

liquids (Albo et al. 2010) as carbon dioxide absorbing solutions.

For liquid-liquid and gas-gas catalytic membrane contactors, see Dittmeyer and Caro (2008) (Fig. 1).

Catalytic diffuser with wettable membrane: The active material is placed solely into the surface layer of an asymmetric membrane. By applying overpressure on the gas side, above the bubble point pressure of the intermediate layer but below that of the surface layer, the gas/liquid contacting plane is established inside the membrane close to the surface layer. In this way, a short diffusion path for the liquid and for the gas reactant is achieved (after Dittmeyer and Caro (2008)).



Contactortype Catalytic Membrane Reactor, Fig. 1 Catalytic diffuser with wettable membrane as an example for a Contactortype Catalytic Membrane Reactor for a solid-catalyzed gas-liquid reaction. By applying overpressure on the gas side, the gas-liquid contacting plane is established inside the membrane close to the surface. In this way, a short diffusion path for the liquid and for the gas is achieved. Reproduced from Roland Dittmeyer, Karel Svajda, Martin ReifA review of catalytic membrane layers for gas/liquid reactionsTopics in Catalysis, 29 (2004), 3-27 reprinted with permission from Elsevier)

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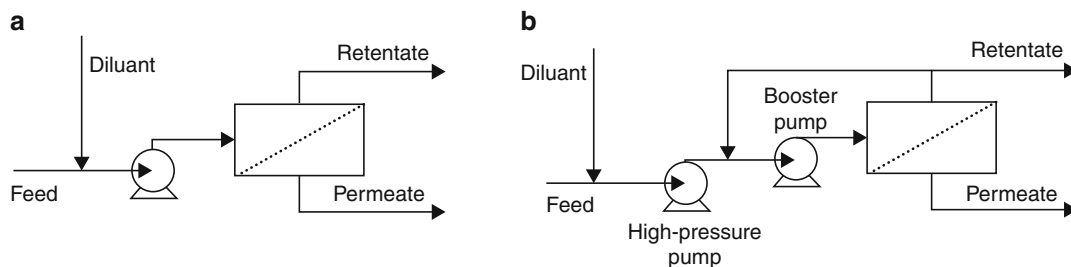
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Continuous Diafiltration: Cocurrent and Countercurrent Modes

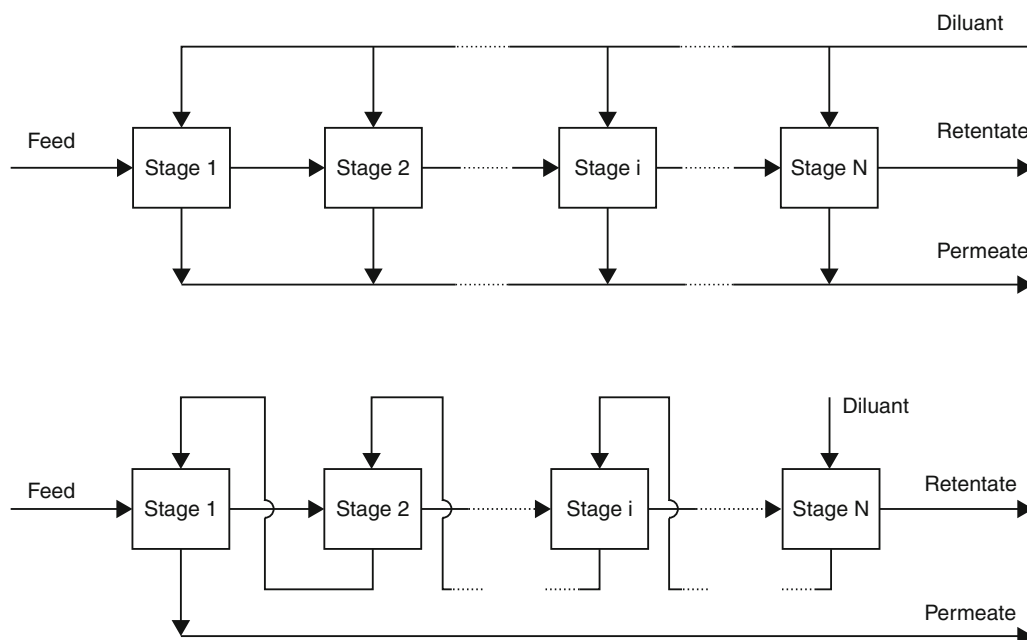
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Continuous diafiltration is a type of diafiltration that accomplishes the selective separation of multiple solutes in a continuous fashion by mixing the feed stream with diluant and pumping it across the membrane with permeate and retentate being removed. The role of diluant addition is to facilitate the separation of membrane-permeating microsolute from the retained macrosolute. This strategy is generally applicable to a variety of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis systems and commonly employed in plants that require large throughputs. Its simplest configuration, known as single-pass diafiltration, is schematically shown in Fig. 1a. Continuous diafiltration, as opposed to batch diafiltration, realizes a steady-state separation in which the product (i.e., the final retentate) is not formed in the feed vessel as filtration progresses, but being continuously withdrawn from the system during the entire course of filtration. In practice, continuous processing employs feed-and-bleed configuration



Continuous Diafiltration: Cocurrent and Countercurrent Modes, Fig. 1 (a) Single-pass continuous diafiltration and (b) continuous diafiltration with partial retentate recycle (feed and bleed)



Continuous Diafiltration: Cocurrent and Countercurrent Modes, Fig. 2 Simplified flow diagram of multistage cocurrent (*top*) and countercurrent (*bottom*) continuous diafiltration

to enhance separation as shown in Fig. 1b. Here, the retentate is split, and a portion of it is recycled back to the cartridge inlet.

Large-scale continuous diafiltration systems operate in multistage arrangement in which a portion of the retentate generated in one stage is used as the feed to the next. These systems can reach higher system recoveries, without exceeding the single element recovery limits. Each stage may consist of several membrane elements

arranged in feed-and-bleed configuration. The two basic concepts of multistage arrangement are the cocurrent (also called crosscurrent) and the countercurrent configurations (Dutr  and Tr g rdh 1994). The former applies fresh diluant at each stage, while the latter uses recycled permeate as diluant as shown in Fig. 2.

Continuous membrane plants are usually designed for both concentration and fractionation purposes. To achieve the twin objectives

of concentrating and purifying a multicomponent feed, the combined application of both concentration mode and diafiltration mode operation is required. Traditional continuous membrane systems consist of a number of stages in series in which consecutive stages are assigned to perform the tasks of pre-concentration, diafiltration, and final concentration (Madsen 2001). Many design variations exist in practice that are primarily achieved by the manipulation of the arrangement of stages within the plant, the number of stages and filtration areas assigned to the various tasks, the amount and the place of fresh diluant addition in the process train, the introduction of bypasses and manifolds, the alteration of permeate recycle ratios, and the appointment of the stages in which permeate is withdrawn from and recycled to (Morison and She 2003, Yee et al. 2007; Mohanty and Ghosh 2008). The selection of optimal diafiltration strategy in continuous processing is very case specific. In general, a reduced consumption of fresh diluant but a larger membrane area is required for the countercurrent approach (i.e., reintroduction of permeate as diluant in the process train) as compared to cocurrent process if the same degree of purification is to be attained (Lipnizki et al. 2002).

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Continuous Electrodeionization

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Continuous electrodeionization is an alternative term for electrodeionization; however, it emphasizes the fact that, in contrast to classical deionization by ionic exchange, this process is continuous.

Continuous Membrane Fermentor (CMF)

► [Cell Recycle Membrane Fermentor](#)

Continuous Stirred Tank Membrane Reactor (CST-MR)

Giuseppe Barbieri

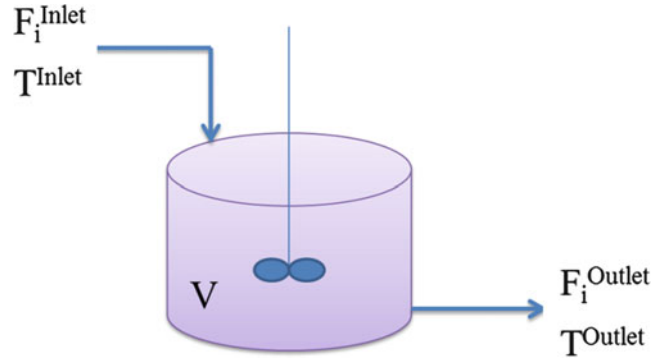
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Before introducing the continuous stirred tank membrane reactor (CST-MR), it is useful/helpful to report about the continuous stirred tank reactor (CSTR).

The continuous stirred tank reactor (CSTR) is an ideal reactor model assuming perfect mixing, with no spatial gradients of any variable such as species concentration, temperature, pressure,

Continuous Stirred Tank Membrane Reactor (CST-MR),

Fig. 1 Continuous stirred tank reactor (CSTR) scheme



etc. The effect of the perfect mixing is the same value for, e.g., concentration, temperature, etc., in any point of the whole reactor volume; and their values are equal to those of the stream exiting the reactor. In addition, the reaction rate has the same value in any point of the reactor. Therefore, this reactor model operating at the lowest reactant concentration and the highest product concentration results in the lowest reaction rate. However, an important effect of perfect mixing is an easy temperature and reaction rate control, which results quite simply. Figure 1 shows a CSTR scheme.

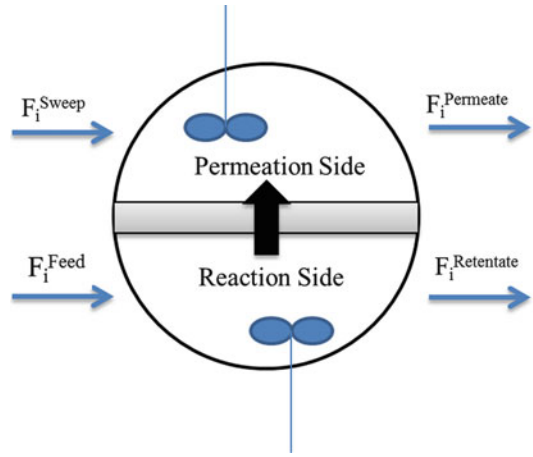
The generic balance equation on the reactor volume will be:

$$\begin{aligned} \text{Inlet} - \text{Outlet} + \text{Generation} \\ = \text{Accumulation} \end{aligned} \quad (1)$$

The mass balance for the component i -th considering a single reaction will be:

$$F_i^{\text{Inlet}} - F_i^{\text{Outlet}} + \sum_{j=1}^{N_{\text{reactions}}} v_{i,j} r_j V_{\text{CSTR}} = \frac{dN_i}{dt} \quad (2)$$

Mass balances provide a set of ordinary differential equations (ODEs), in which the number of moles of component i -th is time dependent. In Eq. 2, F_i^{Inlet} and F_i^{Outlet} are, respectively, the inlet and outlet molar flow of the component i -th, r_i is the reaction rate, N_i is the number of moles, and V is the reactor/reaction volume.



Continuous Stirred Tank Membrane Reactor (CST-MR), Fig. 2 Continuous stirred tank membrane reactor (CST-MR)

In steady-state condition, the mass balance equations fall into algebraic equations:

$$F_i^{\text{Inlet}} - F_i^{\text{Outlet}} + \sum_{j=1}^{N_{\text{reactions}}} v_{i,j} r_j V_{\text{CSTR}} = 0 \quad (3)$$

Equation 3 provides the design equation Eq. 4 for a CSTR in steady-state conditions:

$$\begin{aligned} V_{\text{CSTR}}^{\text{Reaction}} = \frac{F_i^{\text{Inlet}} - F_i^{\text{Outlet}}}{N_{\text{reactions}}} \\ - \sum_{j=1} v_{i,j} r_j \end{aligned} \quad (4)$$

An increase in reaction rate r_i causes a reduction of reactor volume (Eq. 4). The design equation

also provides the reactor volume necessary for obtaining the exit flow rate F_i^{Outlet} , from the feed conditions F_i^{Inlet} , and the reaction rate knowledge.

The energy balance, coupled to mass balance, is given by Eq. 5:

$$\text{Conversion} = \frac{C_p(T^{\text{Outlet}} - T^{\text{Inlet}}) - UA(T^{\text{Outlet}} - T^{\text{External}})}{-\Delta H_{\text{Reaction}}} \quad (5)$$

where C_p is the mean heat capacity, T^{External} is the external temperature, U is the overall heat transfer coefficient, A is the heat exchange area, and ΔH is the enthalpy of the chemical reaction.

This equipment is very commonly used in continuous industrial processes as well as in the plug flow reactor. For reactions of greater than zero order, CSTR always requires a volume larger than that of a plug flow reactor to achieve the same conversion; this is owing to the lower reactant concentrations, as said, at which it operates. Therefore, the use of CSTR is recommended when the desired reaction rate is smaller than that of the side reaction one in order to limit by-product formation.

CST Membrane Reactor

A membrane reactor is a device that combines in one unit a chemical reaction with selective product separation by means of a permselective membrane. The selective removal of products from the reaction side to the permeate side also provides an increase, e.g., of the reaction rate and equilibrium conversion (Fig. 2).

A continuous stirred tank membrane reactor [1, 2] (CST-MR) is a device characterized (1) in addition to the same properties described above

for the CSTR (perfect mixing that has no spatial gradients of species concentration, temperature, pressure, etc.) on both reaction and separation sides (2) by the selective removal of reaction product by the membrane allowing improved performance (see later on) with respect to a CSTR.

The generic mass balance (Eq. 1) is still valid and has to be written down for both reaction and permeation even though another term has to be included: the one taking into account the permeation through the membrane. Therefore, Eqs. 6 and 7 include the permeating flow rate ($A^{\text{Membrane}} J^{\text{Permeating}}$, the product of the membrane area and permeating flux). This term is negative (being mass leaving the reaction volume) on the retentate side and positive (entering the permeation volume) on the permeate one.

Reaction side:

$$\begin{aligned} F_i^{\text{Feed}} - F_i^{\text{Retentate}} - A^{\text{Membrane}} J_i^{\text{Permeating}} \\ + \sum_{j=1}^{N_{\text{reactions}}} v_{i,j} r_j V_{\text{CST-MR}}^{\text{Reaction}} \\ = \frac{dN_i^{\text{Retentate}}}{dt} \end{aligned} \quad (6)$$

Permeation side:

$$\begin{aligned} F_i^{\text{Sweep}} - F_i^{\text{Permeate}} + A^{\text{Membrane}} J_i^{\text{Permeating}} \\ = \frac{dN_i^{\text{Permeate}}}{dt} \end{aligned} \quad (7)$$

The mass balance equations for steady state have an algebraic form:

Reaction side:

$$\begin{aligned} F_i^{\text{Feed}} - F_i^{\text{Retentate}} - A^{\text{Membrane}} J_i^{\text{Permeating}} + \sum_{j=1}^{N_{\text{reactions}}} v_{i,j} r_j V_{\text{CST-MR}}^{\text{Reaction}} = 0 \\ V_{\text{CST-MR}}^{\text{Reaction}} = \frac{(F_i^{\text{Feed}} - F_i^{\text{Retentate}}) - A^{\text{Membrane}} J_i^{\text{Permeating}}}{\sum_{j=1}^{N_{\text{reactions}}} v_{i,j} r_j} \end{aligned} \quad (8)$$

Permeation side:

$$F_i^{\text{Sweep}} - F_i^{\text{Permeate}} + A^{\text{Membrane}} J_i^{\text{Permeating}} = 0$$

$$A^{\text{Membrane}} J_i^{\text{Permeating}} = F_i^{\text{Permeate}} - F_i^{\text{Sweep}} \quad (9)$$

Equation 8 also identifies the reaction volume. It results lower than the CSTR reaction volume owing to the permeation through the membrane.

Therefore, a continuous stirred tank membrane reactor (CST-MR) has a higher performance of a continuous stirred tank reactor (CSTR), specifically, for the following points:

1. Higher conversion owing to the selective permeation through the membrane
2. Higher reaction rate owing to the lower concentration of the products removed by the selective membrane
3. Lower reaction volume at the same productivity owing to the species permeation

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Controlled Delivery

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The benefit of a drug can be enhanced when controlled delivery of a drug to a targeted tissue becomes possible. After release, the drug enters the systemic circulation and distributes according to its relative affinities to all tissues, and only a

small fraction of the drug is delivered to the target site. Accumulation in tissues not associated with drug causes side effects. Controlled delivery to the target tissue eliminates side effects and allows to reduce drug dosing to reach the desired effect. The need for controlled targeted delivery is obvious in chemotherapy, for example, where painful side effects of the drugs on healthy cells can be eliminated by directly delivering the drug to the target cells. Other examples include drug delivery to the eye, lung, brain, and coronary arteries and release of growth and angiogenesis factors from surgically implanted tissue-engineered constructs.

The eye cavity is used to deliver antibiotics and drugs. Ophthalmic inserts made from soluble, insoluble, and bioerodible polymers are currently available. Insoluble inserts can be categorized as diffusional, osmotic, and contact lens. Polyvinyl alcohol, hydroxypropylcellulose, polyvinylpyrrolidone, and hyaluronic acid are commonly used for constructing degradable inserts, while nondegradable inserts are manufactured from ethylene-vinyl acetate copolymers and styrene-isoprene-styrene block copolymers. The contact lenses are not only used for correcting vision but also act as potential drug delivery device by presoaking them in drug solutions. Conventional eye drops are not efficient since most of it is lost due to overflow. To increase drug retention in the cavity and bioavailability, drug delivery product *Ocusert*[®] was developed. In this system, a reservoir filled with a saturated concentration of drug was placed between two membranes that can control release of drug by the partition/diffusion mechanism. This product was placed under the lower eyelid and released drug at constant rate into the tear fluid for up to 1 week. Another commercial product, *Lacrisert*[®] is a soluble insert used for the treatment of dry eye syndrome. The device is composed of hydroxypropyl cellulose and slowly dissolves over 6–8 h to stabilize and thicken the tear film.

In addition to the eye, inserts are also used for targeted controlled delivery of drugs to various tissues. *ATRIDOX*[™] is an FDA-approved product designed for the treatment of periodontal disease. Upon injection into the periodontal cavity, drug delivery depot is formed and delivers the

antibiotic to the cavity. *DUROS*[®] implants are nondegradable, osmotically driven systems and used for the delivery of small drugs, peptides, proteins, and DNA for up to 1 year. *Viadur*[®] is another commercial implant used for treatment of advanced prostate cancer.

Drug-eluting stents were developed to prevent restenosis or reclosing of coronary arteries. In these systems, the implantable metal stents are coated with small amounts of anti-inflammatory and antiproliferative drugs that are released directly into the arterial tissue by dissolution, partitioning, and diffusion. The release rate is influenced by the thickness of the coating, type of the coating material, and diffusivity and solubility of drug in the coating material.

Nanocarriers are alternative systems for targeted controlled drug delivery since they are less cleared than free drugs and they may also have favorable distribution properties into target tissues. Targeting ligands can be incorporated into the nanoparticles, and they permit particles to bind specific cells and promote the cell uptake and release of drug into the cells. Drug-loaded nanoparticles can easily reach to target tumor tissues since tumors have leaky capillaries that permit the passage of nanoparticulates. Microemulsions, liposomes, dendrimers, block polymer micelles, and solid lipid and polymer nanoparticles are typical examples of nanocarriers.

Controlled Drug Release

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Controlled drug release is defined as delivery of a drug to a specific site, in specific time and release pattern. Controlled drug release eliminates over- or underdosing, maintains drug levels in desired range, needs less dosing, prevents side effects, and increases patient compliance. Most of the commercially available systems for controlled release of drugs rely on membranes where drug release is generally controlled by (1) osmotic pumping or

(2) solution–diffusion mechanism. Pills, implants, and patches are commonly used dosage forms to deliver drugs where drug release is controlled by diffusion through a rate-limiting membrane. Pills are prepared by pressing the drug into a tablet and then coating with a water-insoluble or water-soluble polymeric membrane, such as hydroxypropyl methylcellulose, ethylcellulose, povidone, or polyethylene glycol. Tablets are also coated with a membrane to protect drugs against decomposition in the acid environment of the stomach. Commonly used polymers for this purpose are cellulose acetate trimellitate (CAT), hydroxypropylmethylcellulose phthalate (HPMCP), polyvinyl acetate phthalate (PVAP), and cellulose acetate phthalate (CAP). Implants are used to deliver drug at a particular site and contain drug in liquid or powder form in a reservoir surrounded by a semipermeable membrane to allow slow release of the drug. The membrane can be made from a degradable or nondegradable polymer, and the release is controlled by rate of diffusion and degradation. Patches are typical membrane-controlled reservoir systems and frequently used for controlled drug delivery. In ocular patches, a drug is enclosed by two release-controlling polymer membranes, and through diffusion, drug is delivered to the target area. Transdermal patches are used to deliver drugs with low solubility since the skin has a large surface area. The simplest patch consists of a drug-containing reservoir placed between an impermeable backing layer and a membrane. The total resistance to drug permeation is controlled by sum of the resistances in the membrane and the skin. In the case of passive drug transport where the drug concentration difference between the patch and the skin is main driving force, the release rate of the drug may vary significantly from patient to patient due to strong variations in skin permeability. In order to provide an effective rate control and to ensure that drug delivery does not depend on patient or patch position, the permeability of membrane should be less than that of the skin, i.e., the release rate should be controlled by the membrane. To expand the spectrum of transdermally deliverable drugs, chemical permeation enhancers, microneedles, ultrasound, heat, or short- or high-

voltage bursts of electricity are temporarily applied to the skin to disrupt its barrier function. Alternatively, drugs can be delivered by iontophoresis, in which small amounts of electrical current are applied through the skin to allow delivery of charged drug molecules into the body. The device consists of two patches: one of them contains a drug reservoir, while the other patch contains reference electrolyte or gel. The drug placed in the patch electrode which has the same charge as the drug is delivered into the skin by electrostatic repulsion when electric current is applied. The rate of transport of a charged drug during iontophoresis is controlled by passive diffusion, migration due to electric current applied, and electroosmosis due to bulk fluid flow in the same direction as the flow of the counter ions. In addition to classical polymers, intelligent, stimuli-responsive polymers are also used as membrane material for controlling the release rate of drugs through the membrane. For example, hydrogel membranes manufactured from glucose-containing copolymers could respond to the dynamic changes in external glucose concentration, and this response can be used to control the release of insulin through the hydrogel membrane (Obaidat and Park 1997).

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Controlled Release

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Controlled-release technologies are developed to deliver drugs, proteins, pesticides, fragrances, and other bioactive agents at a controlled rate for a desired time period to maintain a constant and effective level of an active ingredient. Controlled-release formulations provide greater

efficacy, convenience, and improved safety by maintaining optimal concentrations of the active ingredient. Many controlled-release technologies operate by diffusion of the active ingredient or water through a rate-controlling membrane and can be classified into four categories: (1) reservoir types, (2) matrix systems, (3) swelling-controlled systems, and (4) osmotic systems.

In reservoir (membrane) systems, the bioactive agent is either encapsulated by two semipermeable membranes or core containing the active ingredient is surrounded by a semipermeable membrane. Diffusivity and solubility of the active ingredient in the membrane are two key parameters that influence the rate of diffusion through the membrane. The size and shape of the active ingredient, the packing density, and the flexibility and crystallinity of polymer chains affect the diffusivity in the membrane. Solubility of the active ingredient in the polymer depends on its interaction with the membrane material.

In matrix (monolithic) systems, the bioactive agent is incorporated in a polymer either in dissolved or dispersed form. When the active ingredients are in liquid form, they are typically dissolved in polymer matrices, while solid ingredients are dispersed in the polymer. Release of the agent occurs by diffusion through the polymer matrix and solubility of the agent becomes a controlling factor.

Osmotic controlled-release systems are reservoir-type systems except that the release of the active agent depends on the diffusion of water into the membrane. In these systems, a semipermeable membrane that is much more permeable to water than to the active agent separates a core with high osmotic pressure from a solution with low osmotic pressure. Water penetration into the core generates a hydrostatic pressure within the core that forces the solution containing the active ingredient out through the membrane. Water permeability of the rate-controlling membrane determines the release rate of the active agent.

Swelling-controlled-release systems are similar to the design of matrix systems and usually consist of an active ingredient dispersed throughout a swellable polymer. In these systems, the active ingredient is not released until the polymer

matrix is swollen since the diffusivity of the active ingredient in the swollen matrix is several orders of magnitude higher than its diffusivity in the unswollen polymer.

Controlled-release systems that are not dependent on diffusion have also been developed. For example, in the case of bioerodible systems, the release rate is controlled by either polymer dissolution or a chemical reaction at the polymer surface; therefore, geometric shape of the release system is important. In pendant chain systems, the active agent is bound to a polymer backbone chain chemically and is released by hydrolytic or enzymatic cleavage. The agent can be attached directly or via a spacer group. The spacer group can be used to affect the release rate and hydrophilicity of the system. In a magnetically controlled-release system, the active agent is uniformly dispersed within a polymer matrix. The system releases the agent in a way typical of diffusion-controlled matrix systems upon exposure to aqueous media. On other hand, when the system is exposed to an oscillating external magnetic field, the release rate becomes much higher.

Various types of polymers have been used in the design of controlled-release systems. The choice of polymer can affect diffusion and partition coefficients in diffusion-controlled systems, the rate of erosion or hydrolysis in chemically-controlled systems, permeation rates of solvents in swelling-controlled systems, and mechanical forces in magnetically controlled systems.

Controlled Release by Membrane

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Many controlled-release systems commercially available now are based on membrane technology. These systems consist of a core containing the drug surrounded by a thin polymer membrane and transport of drug through membrane occurs by a solution-diffusion mechanism. Drug

molecules first dissolve in the membrane and then diffuse from interior part of the membrane to its surface. The diffusive flux through the membrane is described by Fick's first law of diffusion.

$$J = -D \frac{\partial C_m}{\partial x} \quad (1)$$

where D is the diffusivity of drug in the membrane, J is the flux of the drug, and C_m is the concentration of drug in the membrane. At the membrane surface, drug molecules choose to partition into either membrane or surrounding medium. The partition coefficient gives a measure of the preference of drug molecules between two phases. Defining the partition coefficient, K , as the ratio of the concentration in the membrane to the concentration in the solution, flux in Eq. 1 is rewritten as follows:

$$J = -DK \frac{\partial C}{\partial x} \quad (2)$$

where C is the concentration of drug in the surrounding medium. Under steady-state conditions, flux through the membrane is obtained by integrating Eq. 2.

$$J = DK \frac{\Delta C}{L} \quad (3)$$

Controlled-release systems based on membranes usually provide constant release rate as long as the concentration of drug within core is at saturation concentration. Deviations from constant release kinetics occur depending on the storage history of the release device. Time lag is observed when the system is used shortly after being manufactured while migration of the agent from the core into the membrane due to long-term storage causes initial burst effect. Equation 3 clearly shows that the release rate of drug is controlled by diffusivity and solubility of drug in the membrane as well as the thickness of the membrane. Diffusivity of drug in the membrane is influenced by the size and shape of the drug molecules, flexibility, packing density, or crystallinity of polymer chains. Flexibility of polymer chains depends on glass transition temperature and degree of crosslinking of the polymer. Diffusivities are higher in rubbery polymers than those in glassy polymers and

decrease as crosslinking density in the polymer increases. Diffusion takes place in the amorphous phase of the polymers; therefore, diffusivities are lower in more-crystalline polymers than in less-crystalline ones. Solubility of drugs in the membrane depends on the interaction between the polymer and drug. Simply, solubility of drug is higher in polymers containing similar functional groups with those of drug, in addition, solubility decreases with an increase in crystallinity of the polymer. Design of membrane-based controlled-release system for a particular drug requires to choose an appropriate polymer as a membrane material and appropriate thickness to adjust the release rate at a desired level.

Diffusion-controlled release systems are commonly used in commercial products and the most successful example is in transdermal applications. These devices contain the drug either in a reservoir surrounded by a membrane or dispersed in a polymeric matrix and deliver drugs directly through the skin and into the bloodstream. The flux of the drug through the skin is enhanced by using penetration enhancers or electric current. Osmotic controlled-release systems also depend on diffusion of water across a semipermeable membrane. These systems for oral delivery of drugs are prepared by compressing an osmotically active agent into a tablet, coating the tablet with a semipermeable membrane, and drilling a small hole through the coating. As water permeates through the membrane into the tablet, a solution of the agent is pumped out of the hole. Such a device provides a constant rate of release as drug traverses the gastrointestinal tract.

Controlled Release Dose

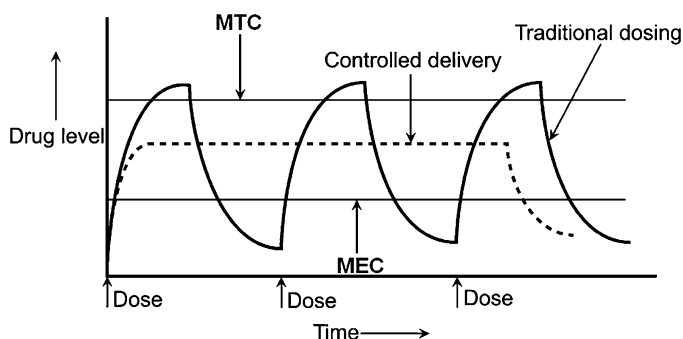
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Controlled release dosage forms are designed to deliver optimum dose of drug at the right time and right place. For an efficient and nontoxic therapy, the drug concentration in plasma should lie within the therapeutic range which is bounded below by the minimum effective concentration (MEC) and above by the minimum toxic concentration (MTC) as shown in Fig. 1. Conventional doses lead to a rapid rise and fall in the drug concentration; therefore, several doses at regular intervals are required to maintain effective levels. After an initial rise, controlled release dosage forms maintain a constant concentration in plasma between MEC and MTC. As a result, several benefits are achieved with these systems including a prolonged therapeutic effect, increasing short half-life of drugs, reduction in dosing frequency and side effects, and improved patient compliance. As shown in Fig. 1, zero-order release allows the best control of plasma concentration and controlled release dosage forms following zero-order release kinetics are usually achieved by using a rate-limiting membrane that is permeable to both drug and water. Osmotic pumping and solution-diffusion mechanism control drug release from membrane systems. In an elementary

Controlled Release Dose,

Fig. 1 The change in drug concentration in blood during drug delivery



osmotic pump, a table or capsule containing drug in the core is surrounded by a membrane that is permeable to water but not drug. After swallowing, water permeated into the core through the membrane dissolves drug, and a constant osmotic pressure gradient established pumps the drug through a hole drilled into the membrane. Zero-order release kinetics are observed so long as a constant osmotic pressure gradient between core and surrounding medium is maintained. When drug concentration falls below its solubility, then rate of drug release starts to decay. To improve the efficiency of osmotic systems, excipients such as water-soluble polymers are added into core, or drug formulation is placed between the water-soluble polymer and the exit orifice. A majority of the coated dosage forms are controlled by solution-diffusion mechanism where the driving force for the diffusional drug release is the drug concentration gradient across the rate-controlling membrane. The drug release rate can be manipulated by varying the membrane thickness and membrane permeability. Permeability can be modified by incorporating soluble additives or pore-forming agents in the membrane material which allows the drug release not only by diffusion but also by osmotic pumping.

To develop a controlled release dosage form, relevant pharmacokinetic parameters for the absorption, distribution, and elimination of a drug as well as its in vivo release profile from the dosage form should be considered. The dosage form should deliver the drug within 24 h which corresponds to the total gastrointestinal tract (GI) transit time in humans. To protect drug from hydrolysis in acidic environment of the stomach, dosage forms are prepared with membranes made from pH-sensitive polymers that are insoluble in acid but dissolve in the neutral or slightly alkaline environment of the gut. Drug is released rapidly if the molecular weight of the polymer is low. If a high molecular weight, water-soluble polymer is used for coating, initially it swells into a gel through which drug diffuses. Following ingestion, the rate of swelling and diffusion through the membrane affect the time for passage of the dosage form through the stomach to the small intestine.

Controlled Release Kinetics

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The release of an active agent from controlled release systems can be categorized into three types: (1) zero-order release kinetics, (2) $t^{-1/2}$ kinetics, and (3) first-order kinetics. In reservoir (membrane) systems, the active ingredient is usually encapsulated between two semipermeable membrane, and the release rate is controlled by diffusion through the membrane. Reservoir systems generally provide a zero-order release where the release rate remains constant until all of the active ingredient has been delivered. The release kinetics from reservoir systems in the form of a flat sheet is described by the following equation:

$$\frac{dM_t}{dt} = ADK \frac{\Delta C}{L} \quad (1)$$

where

M_t = mass of the active agent released up to time t

A = surface area

L = thickness of the rate-controlling membrane

D = diffusivity of the active agent through the membrane

K = partition coefficient of the active agent through the membrane

When the concentration of the active ingredient within the reservoir is less than its saturation value, then the concentration difference through the membrane decreases with time, and first-order release kinetics is observed which can be expressed as follows:

$$\frac{dM_t}{dt} = \frac{C_s ADK}{L} \exp\left(-\frac{ADKt}{VL}\right) \quad (2)$$

where C_s is the saturation concentration of the agent and V is the volume of the reservoir and t is time.

In matrix systems, active ingredients are dissolved or dispersed through a polymer and release rates from these systems decrease with time. Release kinetics from matrix systems containing dissolved active agents is described by a combination of first-order and $t^{-1/2}$ kinetics as follows (Baker and Lonsdale 1974):

$$\begin{aligned} \frac{M_t}{M_\infty} < 0.6 \quad \frac{dM_t}{dt} &= 2M_\infty \left(\frac{D}{\pi L^2 t} \right)^{1/2} \\ \frac{M_t}{M_\infty} > 0.6 \quad \frac{dM_t}{dt} &= \frac{8DM_\infty}{L^2} \exp \left(-\frac{\pi^2 D t}{L^2} \right) \quad (3) \end{aligned}$$

where M_∞ is the total amount of active ingredient initially loaded into the matrix. When active agent is dispersed throughout the polymer, $t^{-1/2}$ kinetics is observed and the release rate is predicted by Eq. 4 (Baker and Lonsdale 1974):

$$\frac{dM_t}{dt} = \frac{A}{2} \left(\frac{DC_{ms}(2C_\infty - C_{ms})}{t} \right)^{1/2} \quad (4)$$

where C_{ms} is the saturation concentration of the active ingredient in the polymer and C_∞ is the concentration of active ingredient initially loaded into polymer matrix.

Osmotic-controlled release which is usually reservoir-type systems follow zero-order release kinetics as long as the osmotic pressure gradient through the membrane is constant. The release rate of the active agent from these types of systems is defined with the following equation (Theeuwes et al. 1983):

$$\frac{dM_t}{dt} = \frac{AP_w \Delta \pi C_{sa}}{L} \quad (5)$$

where P_w is the permeability of water through the membrane, $\Delta \pi$ is the osmotic pressure difference, and C_{sa} is the solubility of the active agent in the membrane.

In swelling-controlled release systems, the release rate depends on the degree of swelling of the matrix which is influenced both by the diffusion of solvent into the polymer and relaxation of the polymer chains. When diffusion is the rate-controlling step, $t^{-1/2}$ kinetics is observed and the

release controlled by relaxation follows zero-order release kinetics (Alfrey et al. 1966).

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Convective Transport

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Introduction

Convective transport (convective flow, bulk flow, convection) may refer to either heat or mass transfer. Convective transport takes place both by diffusion, i.e., the random Brownian motion of individual particles in the fluid, and by advection, in which matter or heat is transported by the larger-scale motion of currents in the fluid. Convective transport is used to refer to the sum of advection and diffusion (Bergman et al. 2011). Convective mass transfer cannot take place in solids, because neither bulk current flows nor significant diffusion can take place in solids, but it can take place in porous solids. Diffusion of heat can take place in solids and is referred to as heat conduction. In the context of membranes, convective flow refers to the transport of fluid (pure solvent or solution) across a porous membrane, which is driven by the applied pressure. Convective transport is the main mode of transport in microfiltration and ultrafiltration processes; it may also contribute to the transport in diffusion dialysis if the pressure is applied. Convective

transport may occur in gas separation membranes if pinholes (defects) are present in the membrane structure, which is undesirable because it diminishes the selectivity of the membrane.

Microfiltration and Ultrafiltration

Ultrafiltration and microfiltration membranes are both considered as porous membranes in which rejection is mainly determined by the size and shape of solute relative to the pore size of the membrane and where the transport of solvent is directly proportional to the applied pressure. For laminar convective flow through a porous membrane, both the Hagen-Poiseuille and the Carman-Kozeny equations can be applied (Mulder 1996). If the membrane consists of straight capillaries, the Hagen-Poiseuille relationship is applicable in which the mass velocity of fluid (N) through the membrane is given by

$$N = \frac{\varepsilon \rho D^2}{32 \mu L \tau} \Delta p \quad (1)$$

where ρ and μ are the density and viscosity of the fluid and ε , D , L , and τ are the porosity, pore diameter, thickness, and tortuosity of the membrane, respectively. For a cylindrical perpendicular pore, $\tau = 1$. If the pore is not straight, the product $L\tau$ represents the actual length of the pore. When membrane has a nodular structure, i.e., it is an assembly of spherical particles, the pores are not cylindrical and straight; Carman-Kozeny equation is then employed (Seader et al. 2011):

$$N = \frac{\varepsilon^3 \rho}{2(1 - \varepsilon)^2 a_v^2 \mu \tau L} \Delta p \quad (2)$$

Equation 2 is obtained by replacing the pore diameter in Eq. 1 by the hydraulic diameter (D_H):

$$D_H = \frac{4A_p}{P} = \frac{4\varepsilon}{a_v(1 - \varepsilon)} \quad (3)$$

where A_p is the cross-sectional area of the pore and P is the wetted perimeter of the pore, which

are then expressed in terms of the specific surface area, a_v , and the porosity of the membrane, ε , (Seader et al. 2011). Equation 2 is obtained by substituting Eq. 3 into Eq. 1.

Equation 2 is sometimes presented in an alternative form (Mulder 1996):

$$N = \frac{\varepsilon^3 \rho}{K(1 - \varepsilon)^2 a_v^2 \mu L} \Delta p \quad (4)$$

where K is the Carman-Kozeny constant, which depends on the shape of the pores and the tortuosity. The commonly used value $K = 5$ implies the membrane tortuosity $\tau = 2.5$.

Gas Permeation

Gas separation requires membranes to be nonporous (e.g., polymeric membranes) or ultramicroporous, i.e., with pores smaller than 0.7 nm diameter (e.g., zeolite and carbon membranes). The pores greater than 2 nm are considered to be defects, because they offer limited (Knudsen flow) or no selectivity (convective flow) for gas separation. The actual mechanism of gas transport through the defects depends on the ratio of the pore diameter (D) and the mean free path of gas molecules (λ):

$$\lambda = \frac{3\mu}{2p} \left(\frac{\pi RT}{2M} \right)^{1/2} \quad (5)$$

where T is the absolute temperature, R is the universal gas constant, P is the pressure, and M is the molecular weight of the gas. If $D/\lambda \gg 1$, i.e., the collisions between gas molecules are more frequent than the collisions with the pore walls, and there is a pressure gradient across the membrane, the convective transport dominates. Since gases are compressible, Eqs. 1, 2, and 4 are applicable in a differential form. Using the ideal gas law, gas density can be expressed by

$$\rho = \frac{pM}{RT} \quad (6)$$

Assuming defects to be straight cylindrical pores, Eq. 1 becomes:

$$N = \frac{\varepsilon D^2 M p}{32 \mu R T} \frac{dp}{dx} \quad (7)$$

At steady state the flux is constant; integrating Eq. 7 from the feed side ($x = 0, p = p_o$) to the permeate side ($x = L, p = p_L$) leads, after rearrangements, (Kesting and Fritzsche 1993) to:

$$N = \frac{\varepsilon D^2 M}{32 \mu R T} \frac{(p_o + p_L)}{2} \frac{(p_o - p_L)}{L} \quad (8)$$

where p_o and p_L are the feed and permeate pressures, respectively.

Dialysis

Diffusion dialysis is a rate-governed membrane process in which solutes are driven across a porous membrane by means of a concentration gradient. When a pressure gradient is applied, in addition to diffusive transport, the solutes may also be transported by the convective flow. The pressure gradient may be applied in order to concentrate the feed, or may be obligatory as a consequence of the geometry of the dialysis device and the desired feed flow rate. On the other hand, in the case of highly concentrated feed, the convective flow may occur from diluted dialysate (permeate) to the feed in response to an osmotic pressure gradient. At steady state, the solute flux (N_s) at a point on the membrane consists of the sum of a diffusive and convective component (Kessler and Klein 1992):

$$N_s = P_m \Delta c_s + N_v (1 - \sigma) \bar{c}_s \quad (9)$$

where P_m is the diffusive permeability of solute, Δc_s is the concentration gradient of solute across the membrane, N_v is the volumetric flux (superficial velocity) of solvent, σ is the reflection coefficient, and $\bar{c}_s$ is the average solute concentration within the membrane. The second term of Eq. 9, $N_v (1 - \sigma) \bar{c}_s$, represents the convective component of the total solute transfer.

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Conventional Ball Milling and Calcination

► Perovskite Powder Preparation Methods

Conventional Pretreatment of Water

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Conventional pretreatment of water is the process and operation applied to the treatment of water or wastewater prior to the feeding of the membrane separation process (MSP).

In membrane processes, the nature of the feed stream is very important, since the presence of colloidal material leads to clogging and adsorption phenomena that alter the mechanisms of operation (Minhalma 2001). Many feed solutions used for the production of potable or industrial process water contain suspended and colloidal matter or soluble salts close to their saturation level. These components cause severe membrane fouling and poisoning. A pretreatment of the feed solution, which guarantees the removal of these materials, is therefore mandatory for a trouble-free operation of membrane separation processes (Strathmann 2004).

Water pretreatment processes are chosen mainly based on the initial type (seawater, brackish water, surface water, wastewater) and quality of the water with respect to the type of foulants (suspended solids, bacteria, organics). Typical methods of pretreatment are the addition of an oxidant (to remove bacteria, algae), coagulation/flocculation (to remove suspended solids), pH adjustment (to prevent scaling), adsorption on activated carbon, and all types of filters such as multilayers and cartridge filters (Nobles and Stern 1995). The integration of flotation processes to coagulation/flocculation steps is also envisaged (Geraldes et al. 2008). Figure 1 presents a summary of the pretreatment processes applied to MSP.

Besides the feed quality, a classification must also be made among different membrane separation processes. Each desalting technology has different requirements for the quality and condition of water entering the process. For membrane processes, the major concerns are membrane fouling and scaling, suspended solid plugging, biological fouling or attack, membrane degradation by oxidation, or other means (Watson et al. 2003).

To lower pressure processes as microfiltration (MF) and ultrafiltration (UF), pretreatment may include chemical coagulation, chlorination, screening, and flow equalization. If the raw water turbidity and/or NOM (natural organic matter) concentration is high, pretreatment will include coagulation, flocculation, and sedimentation. The effect of coagulation is site specific due to interactions between the coagulants, raw water components, and the membrane. In some cases, especially for UF processes, low coagulant doses may cause greater fouling than no coagulation, but higher doses for enhanced coagulation frequently reduce fouling. When iron and manganese are prevalent in the raw water, oxidation may be performed to form a precipitate that can be removed by coagulation. Nevertheless, the use of oxidants requires careful selection of the membrane material, as well as precautions to remove residual oxidant before the membrane treatment step (Davis 2011).

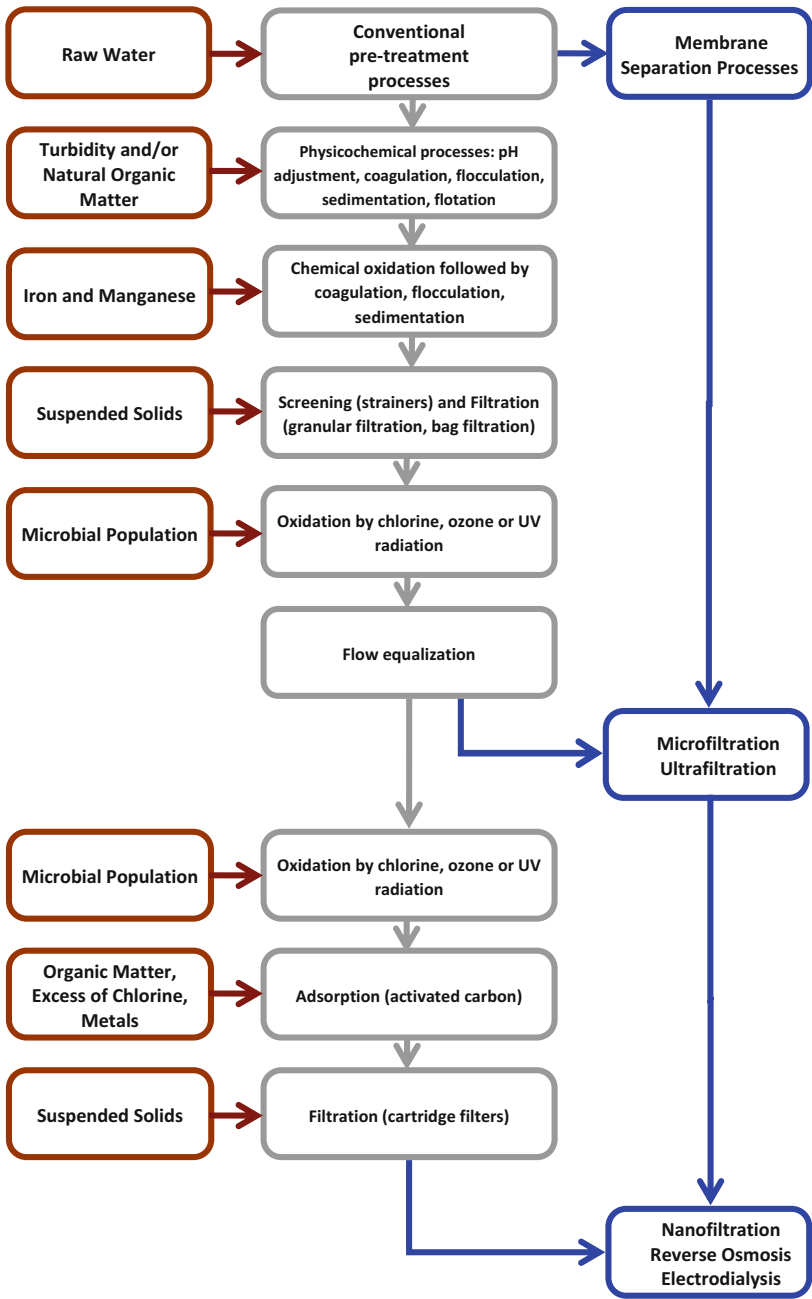
In nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED), the selection of the

pretreatment will also depend on the feed water composition and its variability, but will always comprise a step of solids and turbidity removal and other step of organic compounds removal. Most often, it uses physicochemical processes to remove solids and activated carbon filters to remove organics (Bernardes et al. 2014).

By NF and RO processes, it is important to prevent scaling by silica and sparingly soluble salts such as calcium carbonate and calcium sulfate. Besides silica, calcium carbonate, and calcium sulfate, the other salts that most commonly form scale are barium sulfate, strontium sulfate, and calcium fluoride (Rautenbach and Melin 2004; Baker 2012). Scale control consists of pH adjustment and a softening process. After softening, the effluent is usually further clarified, for example, by sand filtration (Scott 1995). Filtration is used to remove particulate matter that will clog the feed channels or accumulate on the membrane surface. The minimum filtration requirement regardless of the water source is a cartridge filter rated in the 1–25 μm range with a typical rating of 5 μm (Davis 2011). The RO units are fitted with a 0.45 μm cartridge filter, and a sand filter, sometimes supplemented by addition of a flocculating chemical such as alum or a cationic polymer, may be required (Baker 2012). Disinfection by chlorination, ozonation, or UV irradiation may also be required to prevent biofouling (Davis 2011). If chlorine is used, residual chlorine must be removed when polyamide and interfacial composite membranes are used, since these are chlorine sensitive. The development of low-cost MF/UF membrane processes that remove particulate and bacteria has encouraged the use of these membranes as a pretreatment step for RO (Baker 2012).

Although for electrodialysis the water pretreatment is also an important task, comparing to RO, electrodialysis (ED) demands less pretreatment operations. ED only removes ions. Therefore, any bacteria, colloidal material, or silica present in the feed water stream will remain in the product stream. This can be a disadvantage, especially for the production of drinking water, because as only ions are removed, uncharged components such as microorganisms or organic

Conventional Pretreatment of Water, Fig. 1 Summary of the pretreatment processes applied to MSP



contaminants are not eliminated (Bernardes et al. 2014). On the other hand, it brings benefits when, for example, silica is present. Silica occurs in varying concentrations in all natural waters. RO membranes reject silica, but silica is largely unaffected by passage through an ED system. Consequently, silica precipitation is not of concern in

ED plant (Watson et al. 2003). By ED, there is also a possibility of fouling minimization by reversing the polarity of the system several times per hour with electrodialysis reversal (EDR). By reversing the polarity (and the solution's flow direction), ions move in the opposite direction through the membranes, minimizing buildup. This generally

minimizes membrane fouling, decreasing pretreatment requirements in comparison to RO (Bernardes et al. 2014). Since microorganisms are not removed from a feed stream by electrodialysis, most commonly a chlorination of the product water is required. When the concentrate stream has been acidified, the product water pH value must be readjusted. Other measurements may be necessary depending on the feed water composition and required product water quality (Strathmann 2004). Feed waters containing significant quantities of calcium carbonates and bicarbonates are likely to cause precipitation in the concentrate stream at the anion-exchange membrane surface due to pH changes resulting from water splitting which is obtained when the limiting current density is exceeded locally (Strathmann 2004). Organic fouling of ion exchange membranes is one of the major problems in electrodialysis. It is caused by the precipitation of colloids on the membranes, and since most of the colloids present in natural water are negatively charged, it is usually the anion-exchange membranes which are affected. Certain detergents are also the cause of this type of poisoning, which is very difficult to deal with and can best be avoided by a proper pretreatment of the feed solution (Strathmann 2004; Baker 2012). The usual method for removing colloidal material is the pretreatment by coagulation-flocculation and filtration. In this step, some chemicals are used to assist in removal of solids and turbidity as coagulants, flocculants, acids, or bases to adjust pH and oxidizing agent for organic matter degradation. When using membrane process for solid removal, a preliminary step of coagulation may be needed, to increase the efficiency of removal of colloids and/or oxidation. Organic compounds that were not degraded in biological treatment can be removed in activated carbon filters. In this step, it is important to control the generation of fine carbon and, if necessary, adopt operational changes in order to prevent clogging of the cartridge filter and passage into the membrane modules of the electrodialysis. Cartridge filters are also used upstream of electrodialysis as the ultimate protection against suspended solids (Bernardes et al. 2014). Hydrogen sulfide, H_2S , is a frequent

constituent of groundwater along the coast or at other locations where wetlands have existed. Hydrogen sulfide is a by-product of the life cycle of sulfate-reducing bacteria (SRB) that are common in many groundwater systems. Like all gases, H_2S is passed by RO membranes and appears in both the permeate and the concentrate, not being of concern in RO plants. On the other hand, H_2S must be removed from the feed water to ED/EDR plants to prevent oxidation of H_2S in the stack and the resultant membrane fouling by colloidal sulfur. Oxidation occurs by reaction with both the chlorine and oxygen produced by electrolysis in the process. The most common treatment is air stripping, followed by (usually) chlorination to complete the oxidation of the remaining sulfide, and granular filtration (Watson et al. 2003).

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Copolyimide Precursors

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Polyimide Precursors

Polyimides are a class of thermally stable polymers that are often based on stiff aromatic backbones derived from aromatic dianhydrides and aromatic diamines. Polyimides due to their unusual properties are finding a wide range of applications and thus used as precursor (a precursor is a compound that participates in the chemical reaction that produces another compound) to develop materials for various applications. The chemistry of polyimides is in itself a vast area with a large variety of monomers available and several methodologies available for synthesis.

The general formula and chemical structure of polyimide is shown in Fig. 1.

Few of the specialty properties of polyimides include:

High thermal and thermo-oxidative stability up to 400 °C (750 °F)

Excellent mechanical properties, both at room temperature and elevated temperatures

Film- and fiber-forming ability

Excellent adhesive properties, both at room temperature and elevated temperature

Nonflammability – will not support combustion

Applications of Polyimide Precursors

Owing to its excellent chemical and thermal stability, polyimides have wide range of applications

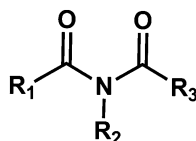
such as in electronics, aircraft, automobile, medical, machining, gas purification, aerospace, and military applications.

For application in electronic and microelectronics industry, fluorine may be introduced to polyimides which reduced the dielectric constant along with retaining the other characteristics mentioned above (Hermciuc et al. 2000). Formation of nanofoam polyimides is a novel approach for reducing the dielectric constant. Basically in nanofoam formation, polyimide polymer replaces with air which reduces the dielectric constant (Hedrick and Charlier 1994). The membrane developed by polyimide containing functional or pendant groups in the backbone of the aromatic dianhydride and/or diamine exhibits good as well as selective gas permeability.

Hyperbranched polyimide (HBPI) precursors were also studied to develop high-performance carbon molecular sieve membranes for improved gas separation applications. It was found that the unique hyperbranched network structure found in HBPI possesses great potential to produce carbon molecular sieve membranes with superior performance (Sim et al. 2013). It is also reported that the membrane produced from the pyrolysis of a hollow-fiber polyimide precursor under suitable conditions has good separation properties when applied to mixed gas pairs, such as O₂/N₂, CO₂/CH₄, and H₂/CH₄ (Jones and Koros 1994). Polyimide-based membranes have been extensively studied for removal of CO₂ particularly from natural gas and found few of them quite efficient (Xiao et al. 2009). Soluble and optically transparent fluorine-containing photoreactive polyimide precursors were developed. These precursors offer high-resolution patterns with aspect ratio of more than 2.0. In these polyimide precursors, the polymers which have a benzophenone segment in the polymer backbone are self-sensitized and show interesting photochemical reactions (Omote et al. 1989).

Polyimide processability is one of the issues associated which cause hurdle to manufacture polyimide parts, such as composites, at costs competitive to other metal parts. Improvement in polyimide processability is essential which could

Copolyimide Precursors,
Fig. 1 Chemical structure
of polyimide



be achieved by reduction in its melt viscosity. Low-molecular-weight end-capped oligomers are potential candidates for the development of polyimide oligomers for improved processability (Smith and Connell 2000; Simone and Scola 2000).

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Copper Removal and Recovery by Supported Liquid Membranes

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Copper is an element that occurs naturally as a metal or as part of sulfide minerals, such as chalcopyrite or bornite, as well as oxides and carbonate ores.

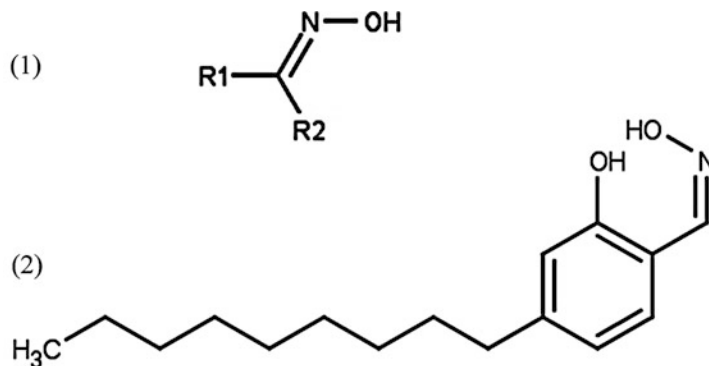
It has been used by human being from the ancient age and today is still extensively applied in many areas that cover a wide variety of different disciplines. It is used mostly as copper metal or copper alloys (electrical devices and wires, coins, pipes, automotive industry, etc.) and also as copper salts (agriculture, water purification, etc.).

This extensive use produces a huge amount of residual wastes containing copper, which may lead to environmental pollution and then justifying a previous treatment to remove and recover copper ions.

Although in general the stability of supported liquid membranes may represent an important difficulty for large-scale operations, recovery of copper was successfully conducted at pilot scale on a hollow-fiber membrane contactor with a surface area of 130 m² (Yan and Kocherginsky 2006).

Copper Removal and Recovery by Supported Liquid Membranes,

Fig. 1 Chemical structure of a ketoxime (1) and 5-nonylsalicylaldoxime (2)



On the other hand, copper is an essential element that takes part in several biogeochemical processes, most of them at very low concentrations. This fact has led to the growing development of hollow-fiber supported liquid membrane systems for analytical sample treatment to the determination of copper traces in environmental samples.

Copper separation though supported liquid membranes may be performed by using a variety of carriers in the organic membrane, mainly organophosphorus acidic compounds (see *Cobalt removal and recovery by supported liquid membranes*) or commercial mixtures of oximes, mostly ketoximes (1) and salicylaldoximes, such as 5-nonylsalicylaldoxime (2), which form complexes with copper ions (Fig. 1).

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Core Shell Particles

► [Membrane Emulsification in Phase Separation for Microcapsule Preparation](#)

Corrosion

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Introduction

Corrosion is the gradual process of wearing, weaning away, and thinning down the metal surface by the fluid with which it is in contact. Millions of dollars are lost every year due to corrosion

of iron and steel. Other metals do corrode. The oxide formed by oxidation does not firmly adhere to the surface of the metal and flakes off easily causing “pitting”. Continued pitting causes structural weakness and disintegration of the metal. Metals such as aluminum form a tough oxide coating onto the surface to prevent corrosion.

In some circles, corrosion has been described as the tendency of a metal to revert to its natural stable state as an ore. The process may involve a second step in which an oxide, hydroxide, or carbonate of the metal may form and deposit at the corrosion site. Thus, corrosion takes place when a metal dissolves in or is disintegrated by water.

Different metals have different tendencies to corrode or not to corrode in the same water. A certain type of water may corrode one metal and not another, but the reverse may be true for another type of water. An excellent method for corrosion control in water heaters is cathodic protection involving the use of a sacrificial anode, usually composed of magnesium or aluminum. Chemical control of corrosion attempts to retard electrode reactions.

The Mechanism and Chemistry of Corrosion Reactions

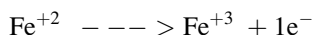
Corrosion reactions are electrochemical in nature. They involve the transfer of charged ions across the surface between a metal and the electrolyte in which the metal is immersed. There are two types of electrode reaction occurring at the metal surface: anodic and cathodic.

Corrosion occurs in the presence of moisture. When iron is exposed to moist air, it reacts with oxygen to form rust. The amount of water <http://www.corrosion.com>, precisely the number of molecules of water, present determines the color of rust varying from black to yellow to orange brown. The formation of rust is a very complex process which begins with the oxidation of iron to ferrous (+2) ions.

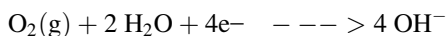
In an anodic reaction, electrons appear on the right-hand side. An example is shown below:



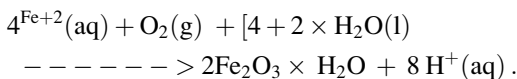
Both water and oxygen are required for the sequence of reactions. Iron (+2) ions are further oxidized to form ferric ions (iron⁺³) ions:



The electrons provided from both oxidation steps are used to reduce oxygen as shown. Cathodic reactions involve electrochemical reduction wherein electrons appear on the left side:



The ferric ions then combine with oxygen to form ferric oxide [iron (III) oxide] which is then hydrated with varying amounts of water. The reduction of oxygen at an electrode will cause a rise in pH due to production of hydroxide ion. The equation for rust formation is



The formation of rust can occur at some distance from the actual pitting or erosion of iron. The electrons produced via the initial oxidation of iron can be conducted through the metal, and the iron ions can diffuse through the water layer to another point on the metal surface where oxygen is available. This process results in an electrochemical cell in which iron serves as anode, oxygen gas as the cathode, and iron solution as “salt bridge”. The

involvement of water accounts for the fact that rusting occurs much more rapidly in moist environment as compared to dry one. The mechanism of corrosion is shown in Fig. 1 below.

Influence of Salt on Corrosion

The presence of salt enhances the rate of corrosion. As the dissolved salt increases, the conductivity of the aqueous solution at the metal surface enhances the rate of electrochemical corrosion. Hence iron and steel corrode more rapidly when exposed to salt or moist salty air near the ocean.

Factors Associated Mainly with the Metal

- Effective electrode potential of a metal in a solution
- Overvoltage of hydrogen on the metal
- Chemical and physical homogeneity of the metal surface
- Inherent ability to form an insoluble protective film

Factors Varying with the Environment

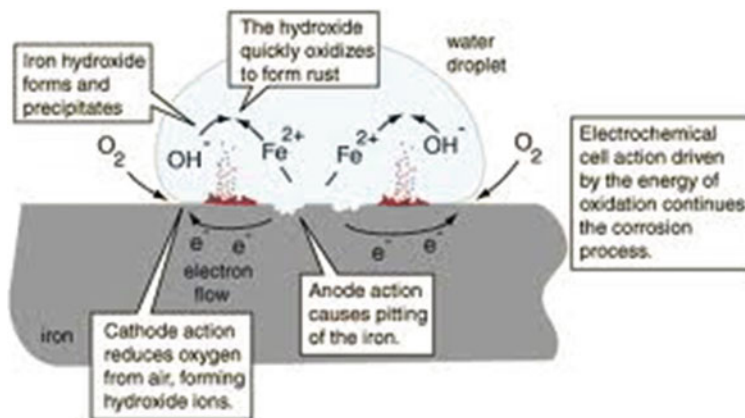
- pH of the solution
- Influence of oxygen in solution adjacent to the metal

Forms of Corrosion

Galvanic Corrosion

This is an electrochemical action of two dissimilar metals in the presence of an electrolyte and an electron conductive path. It occurs when

Corrosion, Fig. 1 The mechanism of corrosion





Corrosion, Fig. 2 Galvanic corrosion

dissimilar metals are in contact. It is recognizable by the presence of a buildup of corrosion at the joint between the dissimilar metals. When aluminum or magnesium alloys are in contact with carbon or stainless steel, galvanic corrosion occurs and accelerates the corrosion of aluminum or magnesium (Fig. 2).

Galvanic Series in Sea Water

(Least Active)

Gold
Graphite
Silver
18-8-3 stainless steel, type 316 (passive)
18-8 stainless steel, type 304 (passive)
Titanium
Thirteen percent Cr stainless steel, type 410 (passive)
7 Ni- 33 Cu alloy
75Ni – 33 Cu alloy
75Ni – 16 Cr – 7 Fe alloy (passive)

Nickel (passive)

Silver solder
M-Bronze
G- Bronze
70-30 cupro-nickel
Silicon bronze
Copper

Red brass
Aluminum bronze
Admiralty brass
Yellow brass
76 Ni-16 Cr-7 Fe alloy (active)
Nickel (active)
Naval brass
Manganese bronze
Muntz
Tin
Lead
18-8-3 stainless steel, type 316 (active)
18-8 stainless steel, type 304 (active)
Thirteen percent chrome stainless steel, type 410 (active)
Cast iron
Mild steel
Aluminum 2024
Cadmium
Aluminum 6053
Galvanized steel
Zinc
Magnesium alloys
Magnesium

Anodic (Most Active) The natural differences in metal potentials produce galvanic differences, such as the galvanic series in sea water. If electrical contact is made between any two of these materials in the presence of an electrolyte, current must flow between them. The farther apart the metals are in the galvanic series, the greater the galvanic corrosion effect or the rate. Metals or alloys at the upper end are noble while those at the lower end are active. The more active metal is the anode or the one that will corrode. The anode must be chosen from the above material list which is lower on the list than the material to be protected.

Control of galvanic corrosion is achieved by using metals closer to each other in the galvanic series or by electrically isolating metals from each other. Cathodic protection can be used to control galvanic corrosion effects.

The following practices are recommended to keep galvanic corrosion to a minimum.

- Avoid the use of widely dissimilar metals in direct contact.

Corrosion,**Fig. 3** Isolation flanges to prevent galvanic

- When dissimilar metals must come into contact, they should be separated by using nonconductive barrier materials, a paint coating, or by plating.
- The anode should be as large as feasible in relation to cathode.
- Coat both the anode and the cathode with the same material.
- Install fasteners that have been dipped in epoxy mastic coatings.
- Seal threaded inserts with epoxy mastic coatings prior to insertion into castings.
- Avoid the use of lock or toothed washers over plated or anodized surfaces.

The scuba tank above suffered galvanic corrosion when the brass valve and the steel tank were wetted by condensation. Electrical isolation flanges (Fig. 3) like those shown on the right are used to prevent galvanic corrosion. Insulating polymeric gaskets are inserted between the flanges, and insulating sleeves and washers isolate the bolted connections.

Pitting Corrosion

The most common effect of corrosion on aluminum and magnesium alloys is pitting. First is noticeable as a white or gray powder, similar to dust, which blotches the surface. When the deposit is cleaned away, tiny pits or holes can be seen in the surface. Passive metals such as

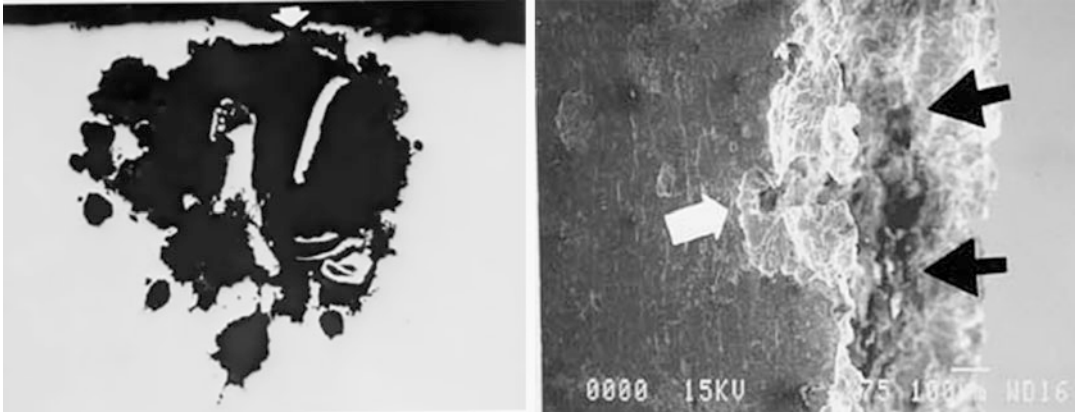
stainless steel resist corrosive media and can perform well over long periods of time. However, if corrosion does occur, it forms at random pits. Pitting may be a serious type of corrosion because it tends to penetrate rapidly into the metal section. It is most likely to occur in the presence of chloride ions, combined with such depolarizers as oxygen or oxidizing salts. Methods that can be used to control pitting include maintaining clean surfaces, application of a protective coating, and use of inhibitors or cathodic protection for immersion service.

Sometimes pitting corrosion can be quite small on the surface and very large below the surface. The figure below left shows this effect common on stainless steel and other film-protected metals. Pitting shown on the right (white arrow) led to the stress corrosion fracture shown by the black arrows (Fig. 4).

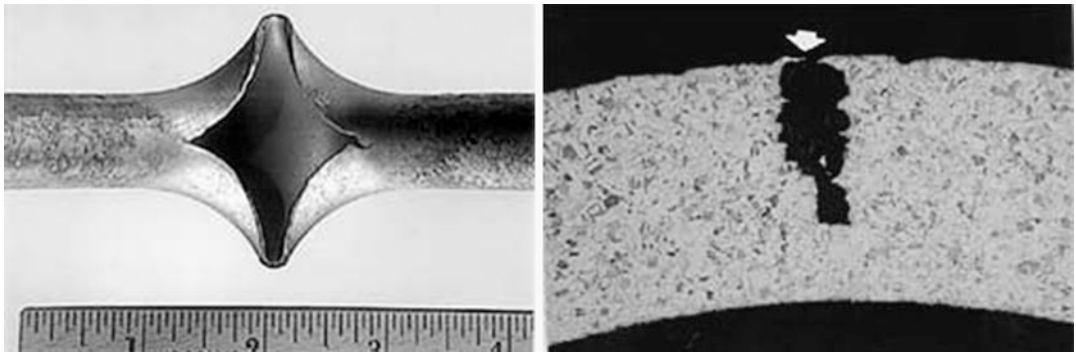
Pitting corrosion can lead to unexpected catastrophic system failure. The split tubing below left was caused by pitting corrosion of stainless steel. A typical pit on this tubing is shown below right (Fig. 5).

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is caused by the simultaneous effects of tensile stress and corrosion. Stress may be internally or externally applied. Internal stresses are produced by nonuniform deformation during cold working,



Corrosion, Fig. 4 Same images for pitting corrosion



Corrosion, Fig. 5 Pitting corrosion for stainless steel tube

by an unequal cooling from high temperatures, and by internal structural rearrangement involving volume changes. Stresses induced when a piece is deformed, those induced by press and shrink fits, and those in rivets and bolts are internal stresses. Concealed stress is more important than design stress, especially because stress corrosion is difficult to recognize before it has overcome the design factor. Few guidelines in avoiding the problem are:

- Use metal alloys at no greater than 75 % of their yield strength and use exotic materials only where they are actually required.
- Avoid assemblies where high-tensile loads are concentrated in a small area.
- Remove stress risers from counter bores, grooves, etc.

Crevice Corrosion

Crevice or contact corrosion is produced at the region of contact of metals with metals or metals with nonmetals. It may occur at washers, under barnacles, at sand grains, under applied protective films, and at pockets formed by threaded joints. Whether or not stainless steels are free of pit nuclei, they are always susceptible to this kind of corrosion because a nucleus is not necessary. Crevice corrosion may begin through the action of an oxygen concentration cell and continue to form pitting. Cleanliness, the proper use of sealants, and protective coatings are effective means of controlling this problem.

Intergranular Corrosion

This is an attack on the grain boundaries of a metal or alloy. A highly magnified cross section of any

commercial alloy will show its granular structure. This structure consists of quantities of individual grains, and each of these tiny grains has a clearly defined boundary that chemically differs from the metal within the grain center. One example of this type of corrosion is in unstabilized 300-series stainless steels sensitized by welding or brazing and subsequently subjected to a severe corrosion environment. Another example of intergranular or grain boundary corrosion is that which occurs when aluminum alloys are in contact with steel in the presence of an electrolyte. The aluminum alloy grain boundaries are anodic to both the aluminum alloy grain and the steel. In the later case, intergranular corrosion of the aluminum alloy occurs. Some austenitic steels are unstable when heated in the temperature range 470–915 °C.

Decreased corrosion resistance in austenitic stainless steels is due to depletion of chromium in the area near the grain boundaries, caused by the precipitation of chromium carbide. This condition can be eliminated by the use of stabilized stainless steel, such as columbium-, tantalum-, or titanium-stabilized stainless steels (types 321/347), or by the use of low-carbon stainless steels. Molybdenum additions as in type 316 stainless steels decrease the sensitivity to and the severity of the intergranular attack.

Intergranular corrosion can be prevented by:

- Select an alloy type that is resistant to intergranular corrosion.
- Avoid heat treatments or service exposure that makes a material susceptible. Normally this occurs with austenitic stainless steels when they are held for some time in the sensitizing temperature range of 470–915 °C (800–1600 °F).
- Apply a protective coating.

Corrosion Removal

Abrasive blasting is the preferred method of removing corrosion; other mechanical methods used are grinding, chipping, sanding, or wire brushing.

Remove corrosion by *mechanical method* such as wire brushing or abrasive blasting as

appropriate. Failure to adequately clean all residues will permit corrosion to continue. Light corrosion may be removed from thin members – ducts and tubing – with a nonwoven, nonmetallic abrasive mat in accordance with MIL-A-9962 or number 400 aluminum oxide or silicon carbide grit abrasive paper or cloth. Do not use steel wool.

Chemical Method

Chemical corrosion-removal methods can be used when no danger exists that the chemical used will become entrapped in recesses and when there is no danger that adjacent material will be attacked. The chemical method should be used on complex shapes and machined surfaces. Chemical rust removers are of two types: acid or alkaline. The acid type is used in removing rust and black oxide by immersion or brush application. This is a phosphoric acid-type remover and must not be used on high-strength steel heat treated above 1.24 gigapascals (GPa) tensile strength due to possible stress corrosion or hydrogen embrittlement problems. The alkaline type (sodium hydroxide base) is suitable for use by immersion only. Use on machined surfaces where a dimensional change would be objectionable.

Scale conditioners are used as necessary to facilitate oxide scale removal by acid cleaning. The use of scale conditioners shall not cause pitting, intergranular attack, or reduction of mechanical properties below the minimum values as specified in the applicable material specification for the alloy, gage, and heat-treat condition.

When acid cleaning is used to remove heat-treat scale, flux, corrosive media, stains, and other contaminants, it shall be within the limits specified. Acid cleaning shall not result in intergranular attack that would be detrimental to the fabrication or use of the material or part. Acid cleaning shall not result in pitting or smutting, which will not be readily removed by subsequent processing. Cleaning shall be accomplished in the following bath:

1. Nitric acid (HNO_3) (42 Baume)
225–375 kg/m³

2. Hydrofluoric acid (HF) or NH_4HF_2 9–52 kg/m³
3. Temperature: room 60 °C (140 °F)
4. Metal content, HF ratio = 1: 1.8 (replenish bath when the metal concentration >1 part of metal to 1.8 parts of HF)

Stainless Steel Alloys

Stainless steels owe their inherent corrosion resistance to a condition known as passivity – as a result of the presence of their oxide films called “passive films.” Under favorable conditions, such films are protective; however, unfavorable conditions deficient in oxygen will destroy the films and leave the surface in an “active” state with corrosion resistance comparable to carbon steel. The presence of hygroscopic salt deposits, dirt, dust, and other foreign matter all serve to destroy passivity. Underground exposure of bare stainless steel will result in unacceptable quality. Where localized corrosion occurs, rapid penetration (pitting) at the point of initiation can occur as an electrolytic cell is formed between the large cathodic (passive) area and the small anodic area under attack. This attack is particularly severe in the presence of halide salts. Localized attack will also occur in crevices, such as under sleeves on tube fittings.

Superior resistance to pitting is attainable with type 904 L unified numbering system (UNS) N08904 stainless steel over other commonly used steels. However, this is only a matter of degree and localized attack can still occur. Maintaining clean surfaces will greatly reduce the opportunity for corrosion, regardless of the alloy employed.

Typical Problem Areas

- **Sharp edges.** Sharp edges of metal structures will often be deficient of proper coating thickness; sharp edges should be rounded when possible with the National Association of Corrosion Engineers (NACE). A stripe coat or brush coat of primer prior to spray will assist in getting adequate coverage.
- **Nuts and bolts.** Premature coating failure and corrosion on nuts and bolt heads are common and can be reduced by conscientious surface

preparation prior to application of a protective coating. A brush coat of primer prior to spray will ensure adequate coverage.

- **Tube clamps.** Carbon steel clamps for interior applications are either zinc plated or painted. Stainless clamps shall be used for all exterior applications. Corrosion at the interface between the stainless steel tubing and the clamp can occur due to dissimilar metal and crevice corrosion. Corrosion at the interface between tubing and clamps is controlled by application of protective coatings.
- **Unistrut channels.** Use of unistrut channels should be avoided in exterior locations. When the exterior use of unistrut cannot be avoided, selection of appropriate material shall be utilized, such as stainless steel or fiber glass. Where corrosion is noted, mechanically clean the member to remove corrosion products followed by application of a zinc-rich coating.

Stainless Steel Components

General Stainless steel, although very corrosion resistant, is susceptible to localized corrosion (e.g., pitting, crevice corrosion, etc.) when exposed to marine environment. A mistake frequently made is to conclude that the corrosion noted on stainless steel tubing and bellows is only superficial. This conclusion is improperly reached when removal of external corrosion products leaves the surface in a condition that appears almost like new except for what appears to be a very tiny pit. A cross section taken through such a typical pit frequently discloses a void considerably greater in diameter than the surface pit diameter. Failure to arrest the apparent superficial corrosion will result in ultimate penetration of thin wall members.

Application of Protective Coatings

Stainless steel tubings shall be treated in the following way:

- Accumulated dirt and oil shall be removed by rinsing with water followed by rinsing with methyl ethyl ketone (MEK).

- Remove corrosion products by mechanical means, such as power tool cleaning or hand-tool cleaning.
- Clean surfaces with methyl ethyl ketone using clean rags.
- Apply by spraying, brushing, or dipping 75 μm (3 mils) minimum of the coating Aerocoat AR-7 manufactured by B.F. Goodrich.

Tubing assemblies shall be abrasive blasted. When tubing assemblies are in close proximity to carbon steel structural members that are to be abrasive blasted and coated with inorganic zinc-rich primer, the tubing assemblies shall be similarly treated.

- Using clean rags, accumulated dirt and oil shall be removed with water followed by wiping with methyl ethyl ketone.
- Apply a zinc-rich coating in accordance with the manufacturer's recommendations to a DFT (dry film thickness) of 100–150 μm (4–6 mils).

Cathodic Protection

Cathodic protection (CP) is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell. CP is carried out by connecting the metal to be protected with a piece of another more easily corroded “sacrificial metal” to act as the anode of the electrochemical cell. The sacrificial metal then corrodes instead of the protected metal. For structures where passive galvanic CP is not adequate, like in long pipelines, an external DC electrical current is applied. Cathodic protection systems are used to protect a wide range of metallic structures in various environments. Common applications are steel water or fuel pipelines and storage tanks such as home water heaters, steel pier piles, ship and boat hulls, offshore oil platforms and onshore oil well casings, and metal reinforcement bars in concrete buildings and structures. A common application is in galvanized steel, in which a sacrificial coating of zinc on steel protects them from rust.

Cathodic protection can, in some cases, prevent stress corrosion cracking.

Applications Pipelines are routinely protected by a coating supplemented with cathodic protection. An *ICCP* – *impressed current cathodic protection* – system for a pipeline would consist of a DC power source, which is often an AC-powered rectifier and an anode, or array of anodes buried in the ground (the anode ground head)

Ships: cathodic protection on ships is often implemented by galvanic anodes attached to the hull, rather than using ICCP. Since ships are regularly removed from the water for inspections and maintenance, it is a simple task to replace the galvanic anodes. Galvanic anodes are generally shaped to reduced drag in the water and fitted flush to the hull to also try to minimize drag.

How to Prevent Metal Corrosion

- Choose products that are made of noncorrosive metals like stainless steel and aluminum.
- Maintain a dry environment using appropriate moisture barriers.
- Ensure the electrical connections are clean.
- On a car or truck, apply a thin coating of petroleum jelly after cleaning the terminal.
- Coat metals with oil, paint, grease, or varnish because it can prevent corrosion.
- Make use of cleaning agents like soaps, solvents, emulsion compounds, and chemicals to efficiently get rid of oil, grease, dirt, and other unwanted foreign deposits and follow the correct procedures in applying them.
- A mixture of cola and baking soda paste will remove metal corrosion on car batteries.
- To prevent soil corrosion, install correctly copper or copper alloy plumbing underground. The main causes of copper corrosion are poor drainage and moisture. A loose layer of backfill such as limestone or pea level must be put down in the trench before laying copper pipes.
- Galvanizing also provides metal corrosion protection. This is the process of giving a thin coating of zinc or steel material by immersing

the object in a bath primarily of molten zinc. Galvanizing is an efficient way to protect steel because even if the surface is scratched, the zinc still protects the underlying layer. This process is widely used in the auto industry.

Summary

Corrosion is effectively controlled by cathodic protection or by appropriate selection of inhibitors, provided the chemical and electrical conditions are scientifically monitored. Understanding of the mechanism is the key in handling the condition of the metals and structures. Every scenario is site specific and needs to be addressed on its associated factors of pH of the medium, environment, and temperature. Accordingly adopt the right protection techniques out of the available:

- Removal of oxidizing agent
- Prevention or inhibition of surface reaction
- Application of protective coatings – organic/metallic/nonmetallic
- Modification of the metal or the surface conditions

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Co-sintering Method for Ceramic Membrane Preparation

Zhaoliang Cui

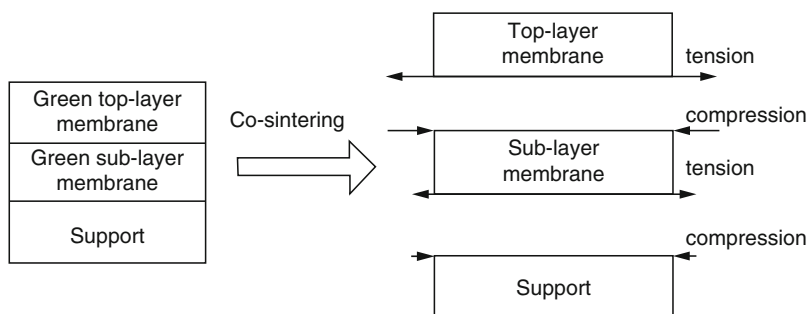
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Co-sintering method for ceramic membrane preparation. Conventionally, a multilayer ceramic membrane can be obtained by repeating the coating procedure. But the complicated, time- and energy-consuming production process, which generally comprises several sequential steps, induces high price. Obviously, reducing or combining steps is expected to cut production time and costs and thereby ceramic membrane price. As a method for fabrication of multilayer structures, the co-sintering process has attracted increasing attention due to simple preparation process and low production cost, including ceramic membranes (Lindqvist et al.) (Lindqvist and Liden 1997).

As shown in Fig. 1, in co-sintering process, a drying and a sintering step are eliminated, resulting in a faster and cheaper preparation. Another benefit of this process is the excellent linkage between the support and the intermediate layer, as well as the uniform and controlled thickness of the intermediate layer (Lindqvist et al.) (Lindqvist and Liden 1997). However, the thermal mismatch of each layer is a common and key problem during the co-sintering process. In a

Co-sintering Method for Ceramic Membrane Preparation,

Fig. 1 Co-sintering process (Feng et al. 2007a)



multilayer ceramic membrane, each membrane layer, which is made from ceramic powders with different compositions and particle sizes, exhibits different sintering behavior. Therefore, it is important to ensure the sufficient sintering of each membrane layer and also ensure the high bonding strength of each membrane layer in an asymmetric ceramic membrane (de Jong et al. 2004). For α -alumina membranes, too large shrinkage mismatch between two membrane layers, which occurs when co-sintering at 1,450 °C, causes many defects such as cracks and big pores. Moderate shrinkage mismatch existed when co-sintering at 1,300 °C, which can bring compressive stress in the sub-layer membrane, is beneficial to the whole co-sintering process (Feng et al. 2007a, b).

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Cost-Effective Gas Separations

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The separation of gases is an essential unit operation for a large number of chemical processes. The membrane-based gas separation processes are one of the several options available to the process engineers. Therefore, a membrane gas separation process has to compete with the more established gas separation processes such as cryogenic distillation, absorption, and adsorption. Although gas

separation membranes can be used for a wide range of applications, they have generally found their applications only in a few niche markets. These applications are listed in Table 1. In these markets membranes may not be the most cost-effective gas separation process but offer other advantages which make a compelling case for their use. These non-tangible benefits of the membrane gas separation processes are listed in Table 2.

Two necessary but not sufficient properties of the gas separation membranes are its selectivity for a given pair of gases and the gas permeation rate of the faster gas. The membrane selectivity is associated with the energy usage and/or product loss (energy cost), and the gas permeation rate is a measure of the membrane area needed (capital cost) for a given separation. Thus, these two factors have a major impact on the economic viability of a given membrane for a separation of interest. In addition, these two properties dictate the geometry of the membrane (tubular, hollow fiber or flat sheet), design of the membrane module, configuration of the membrane cascade (single stage or multiple stages), and process flow schemes (parallel, series, recycle, sweep, etc.) (Agrawal

Cost-Effective Gas Separations, Table 1 Commercial applications of gas separation membranes

Nitrogen production from air
Air-drying
H ₂ /CO adjustment in synthesis gas
H ₂ recovery in ammonia synthesis
H ₂ recovery in petrochemical processes
Acid gas removal from natural gas
Recovery and recycle of olefins in olefin polymerization process

Cost-Effective Gas Separations, Table 2 Benefits of membrane gas separation process

Lower foot print and weight
No moving parts (except for compressors)
Remote operation
Easy turnup/turndown
Portability
No open flames

and Xu 1996). They also determine the operational mode of the membrane such as pressurized feed gas with or without intermediate compression or membrane module operation with vacuum on the permeate side while keeping the feed gas a little over the atmospheric pressure. All these factors contribute to the bottom line economics of the gas separation process.

The life of the membrane and the replacement cost of the membrane module are a major contributor to the cost effectiveness of the membrane gas separation. For commercial membrane gas separations, the membrane life varies from application to application. A major contributor to the life of the membrane is its chemical compatibility with the feed gases. A membrane material may be chemically inert to the major gases in the feed gas, but the trace impurities present in it may damage the membrane over a period of time by causing compaction or other defects. In those cases, the feed gas may be pretreated to remove trace impurities before the gases are fed to the membrane separator. The type and extent of cleaning of the feed gases has a major bearing on the overall cost of gas separation by membranes.

Hybrid processes consisting of a membrane separation process with a conventional gas separation process sometimes offer a more cost-effective solution for gas separation. Two examples of these processes which are commercially used are in production of high purity nitrogen and in the treatment of natural gas. Air separation membranes have selectivity limitations; therefore, they are not best suited to produce high purity nitrogen. However, when a membrane air separation process is combined with an adsorption process, membrane separation produces 95–99 % nitrogen from which final traces of oxygen is removed by adsorption process (Choe et al. 1987). The second application of hybrid process is for the removal of acid gases from the natural gas. Here, a hybrid process consisting of acid gas selective membrane followed by an amine scrubbing process offers a more economical process for natural gas upgrading (Baker and Lokhandwala 2008).

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Further Reading

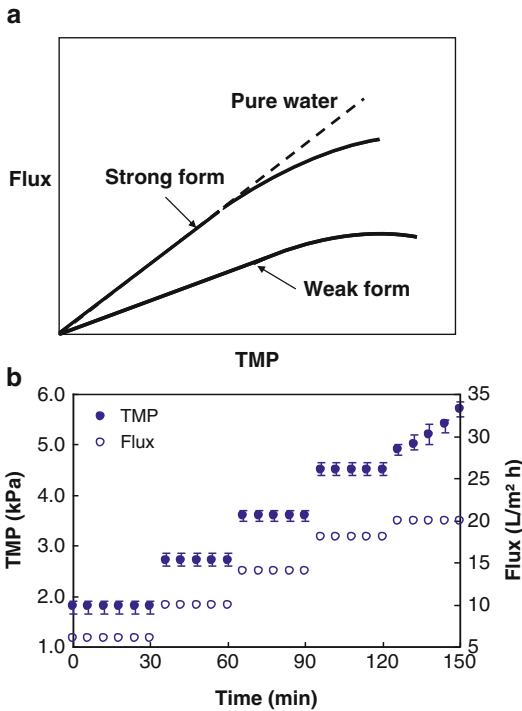
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Critical Flux

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The reduction in the permeate flux with time is a major problem in many pressure-driven membrane processes due to membrane fouling. This problem should be solved before the membrane processes are economically or technically viable. To control membrane fouling and maintain sustainable operation, the concept of critical flux was first introduced in 1995 (Field et al. 1995). The critical flux is defined as the flux below which flux decline with time does not occur, while fouling is observed above it. The supercritical flux fouling is ascribed to the fact that the convection of foulants toward the membrane by the permeate drag flow exceeds the back transport velocity of material from the membrane induced by shear and Brownian diffusion. Since then, the critical flux has been extensively applied to membrane processes from microfiltration (MF) to reverse osmosis (RO). Nowadays, the critical flux concept is well accepted by both scientists and engineers.

There are two forms of the critical flux: strong and weak form (Fig. 1a). In the strong form, the flux obtained during subcritical flux is equated to the clean water flux obtained under the same conditions. The strong form of critical flux is the point, at which the transmembrane pressure (TMP) starts to derive from the pure water line.



Critical Flux, Fig. 1 The strong and weak forms of critical flux (a) (Field et al. 1995) and critical flux measurement by the flux-step method (b) (Li et al. 2013)

In the alternative weak form, the flux–TMP relationship is below that of the pure water line, but increases linearly with pressure. The weak form of critical flux is the point at which this line becomes nonlinear. The difference between the two forms is that the strong and weak forms of critical flux are mainly caused by reversible and irreversible fouling, respectively. Therefore, the weak form of the critical flux is typically observed with the real effluents which contain many solutes of various molar masses.

However, the main drawback of this concept is that the determination of critical flux values cannot be theoretically predicted, but only experimentally measured by time-consuming experiments. The reason is that critical flux value is dependent on various factors, such as the characteristics of the membrane (pore diameter, porosity, and material), suspension system (nature, particle size distribution in relation to pore size distribution, and concentration), and the hydrodynamic and filtration conditions. Thus, a number of measurement methods for critical flux has been proposed (Table 1). The differences among these various methods are the quality (accuracy and reliability) and cost (length of experiment and complexity). The critical flux has mainly been obtained from flux–TMP measurements often by flux or pressure stepping (Fig. 1b). The mass balance method could be a useful complement for these methods with a determination of deposited mass. However, for complex suspensions, the analysis of the criticality via fouling rate has become increasingly common. Also the critical

Critical Flux, Table 1 Measurement methods for critical flux (Bacchin et al. 2006)

Methods	Advantages	Disadvantages	Suitability
Flux–pressure profile: deviation from linearity	Simplicity	Subjective and no link with reversibility	Feeds with low osmotic pressure
Flux or pressure vs. time: flux stepping	With up and down steps, fouling hysteresis found	Points of transition to irreversibility can be missed	Feeds with low osmotic pressure
Flux or pressure vs. time: flux cycling	Rigorous when allowance made for osmotic pressure	Time consuming and complex	All feeds
Direct observation through membrane (DOTM)	Direct observation of flux giving deposition	Soluble deposition not visible	Particulate feeds
Mass balance	Linked to complementary parameter, the deposited mass	Soluble deposition not visible	Particulate feeds
Determination by fouling rate analysis	Identify a point of sustainable flux	Subjective and no link with reversibility	All feeds

flux can be deduced from the observation of particle deposition (or their absence) on the membrane surface by direct observation through the membrane (DOTM). However, the industry system often operates at an acceptable fouling rate to achieve a higher permeability. The industrially acceptable flux is determined from economic considerations, and then its value would change as the balance between capital and running costs. Overall, the critical flux provides an important guide for the appropriate operating flux.

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Cross-Flow Filtration

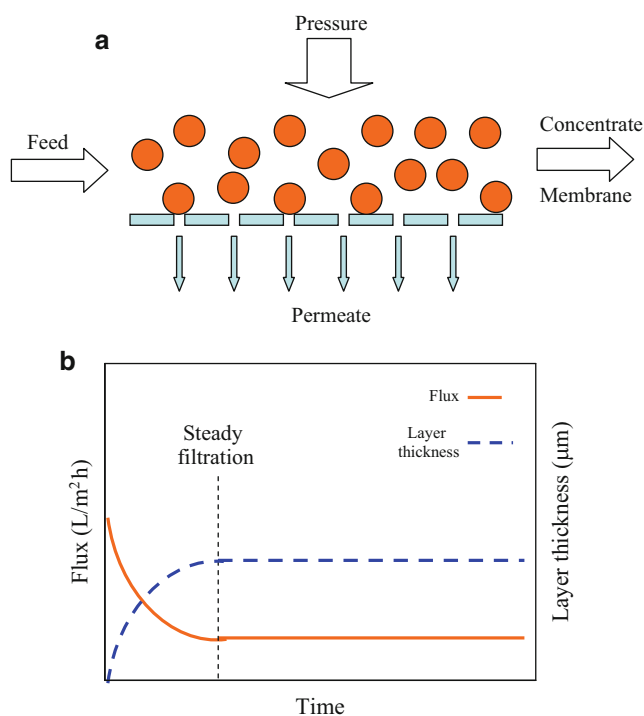
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The conventional pressure-driven membrane processes in liquid separation can be divided into two modes: dead-end filtration and cross-flow filtration. If there is no retentate stream, then the operation is termed “dead-end filtration.” If the retentate continuously flows from the module outlet, then the operation is termed “cross-flow filtration.” In the cross-flow filtration, the fluid feed stream runs tangential to the membrane surface, leading to a pressure differential across the membrane. This causes some of the particles to pass through the membrane. And the remaining particles continue to flow across the membrane. In contrast to the dead-end filtration technique, the

Cross-Flow Filtration,

Fig. 1 Schematic diagrams of cross-flow filtration (a) and representation of the steady filtration flow (b)



shearing effect caused by cross flow can sweep the deposited particles toward the concentrate or retentate side so that the cake layer remains relatively thin (Fig. 1a). In the case of cross-flow filtration, a cake layer will be built up gradually. After some time, a steady filtration state is obtained for a long time as shown in Fig. 1a. This fact is due to the equilibrium between the transport of particles to the cake layer and the back transport of particles into the feed stream. Consequently, the cross-flow filtration is commonly employed for the large-scale industrial membrane filtration process.

The permeate flux is governed by the general filtration equation (Darcy’s law) given as

$$J = \frac{\Delta P}{\mu \cdot R_h} \tag{1}$$

where J ($\text{m}^3/\text{m}^2/\text{s}$) is the permeate flux, ΔP (Pa) is the applied pressure, μ (Pa.s) is the solvent viscosity, and R_h (m^{-1}) is the hydraulic resistance.

Certainly, many parameters of cross-flow filtration play a key role in filtration performance. As summarized in Table 1, the parameters influencing filtration performance cover hydrodynamics and operating conditions, membrane characteristics, as well as the fluid characteristics. For example, on the basis of Darcy’s law, the operating conditions (transmembrane pressure, cross flow, and temperature) are directly related to the permeate flux. Membrane characteristics (pore size, surface free energy, hydrophilicity/hydrophobicity, etc.) and fluid characteristics (pH,

particle size, interactions, etc.) will strongly impact the physicochemical interactions that occur between the fluid constituents and the membrane surface as well as between these constituents. Therefore, the goal of membrane technologists is to use appropriate membrane material, module configuration, system design, and operating conditions to achieve the most economical process.

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Cross-Flow Membrane Bioreactor

► [Aerobic Membrane Bioreactor](#)

Cross-Flow Membrane Module

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Synonyms

[Flat sheet membrane module](#); [Plate and frame module](#)

Cross-Flow Filtration, Table 1 Summary of the parameters influencing cross-flow filtration performance (Rayess et al. 2011)

	Parameters
Operating conditions	Transmembrane pressure, permeate flux, cross-flow velocity, and temperature
Membrane characteristics	Pore size, porosity, hydrophilicity/hydrophobicity character, and surface free energy
Fluid characteristics	Physicochemical interactions (electrostatic, polar, etc.), pH, ionic strength, suspension concentration, and suspension size

In order to apply membranes in a technical scale, large membrane areas normally are required. The smallest unit into which a membrane area is packed is called a module (Mulder 1997). The earliest designs were based on simple filtration technology and consisted of flat sheets of membrane held in a type of filter press (Baker 2004). Modules containing only one membrane, which are mostly used in laboratory scale, are cross-flow membrane modules. If several membranes are

used, these modules are called plate and frame modules.

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Cross-Link

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The reticulate polymer formation processes by the interactions of linear or branched polymer chains using the chemical modification or physical modification are defined as “cross-link.” Cross-link is mainly divided into two types including chemical cross-link such as polycondensation or polyaddition cross-link (Beryozkina et al. 2009; Luis et al. 2012) and physical cross-link such as heat or photo cross-link (Chujo 2010; Farrell et al. 2005). Chemical cross-link is defined as the interaction process of linear or branched polymer chains by using the covalent bond among the functional groups of the polymers and cross-linking agents. Most of the chemical cross-linking agents are small molecular compounds with the molecular weight of 200–400, which have two or more functional groups such as amine group (Bernardo et al. 2009). Physical cross-link is the interaction process of linear or branched polymer chains by using the physical interaction such as van der Waals forces and hydrogen bond among the functional groups of the polymers and cross-linking agents. After cross-linking, polymer properties such as the mechanical strength, elasticity, solvent resistance, and permeate selectivity could be improved (Bernardo et al. 2009; Beryozkina et al. 2009; Chujo 2010; Farrell et al. 2005; Luis et al. 2012).

In the membrane fabrication process, cross-link is also mainly divided into two types including chemical cross-link and physical cross-link. Hydrogen bond cross-link is a special physical cross-link. Different from other cross-links, the functional groups of the polymer will be not depletion after the hydrogen bond cross-link (Basu et al. 2010). Compared with the covalent bond, the hydrogen bond energy is smaller, and the bond length is longer, which is a weak link. However, a large amount of hydrogen bonds can stably exist in the membrane at low pressure due to the strong physical interactions (Basu et al. 2010). In the membrane fabrication process, chemical cross-link and physical cross-link often make the gap space between the polymer chain segments smaller and limit the vibration of the polymer chain segment, which are main ways to improve the selectivity (rejection) of the permeate (Luis et al. 2012; Zhao et al. 2006; Basu et al. 2010; Qiao et al. 2013; Kim et al. 2000). However, most of the cross-linking processes will make the membrane structure densification and may be not favorable for the permeance (flux) increase of the permeate in the membrane process (Luis et al. 2012; Basu et al. 2010; Zhao et al. 2006). Fortunately, in the recent studies, the cross-linking agents with functional groups such as amine group used to modify the polymer could simultaneously improve the selectivity and permeance of the permeate in the gas separation membrane process (Qiao et al. 2013).

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Cross-Linkable Copolymer Membranes

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Cross-linkable copolymer membrane is one of the most extensively used polymeric membranes, such as gas separation membrane, pervaporation membrane, proton exchange membrane for fuel cell, and stimuli-responsive membrane.

Cross-linkable copolymer is a kind of copolymer bearing the cross-linkable groups in the chain end or the side-chain of one specific unit. Amino group, epoxy group, carboxyl group, silane group, and vinyl group are the common cross-linkable groups. Furthermore, some specific cross-linkable groups could be incorporated in the copolymer matrix in terms of actual demands. Cross-linking reaction can be carried out through thermal/photo initiation by oneself or chemical reaction with other cross-linking reagents. Various properties of copolymer such as thermal stability, mechanical strength, and chemical resistance could be improved after cross-linking. As a novel polymeric material, cross-linkable copolymers are widely used for fabrication of stimuli-responsive polymer vesicles (Li and Keller 2009) and organic

light-emitting diodes (Segalman et al. 2009). Moreover, cross-linkable copolymers are the favorable polymeric membrane materials owing to their diversity.

Cross-linkable copolymer membranes exhibit the characteristics of structure control and property tunability due to the versatility of comonomers and cross-linkable groups of cross-linkable copolymers. Cross-linkable copolyimide is a class of fine membrane materials for CO₂ separation. Most of the glassy polymers suffer from CO₂-induced plasticization at high CO₂ partial pressure (Bos et al. 1999). However, cross-linked copolyimide reveals excellent CO₂ plasticization resistance due to the formation of rigid polymer networks (Vanherk et al. 2013). End-group cross-linkable sulfonated copolymers (poly(arylene ether ketone), poly(ether ether ketone), etc.) are the predominant proton exchange membrane materials for fuel cell, which often provide improved proton conductivity and reduced water uptake via proper cross-linking (Jones and Roziere 2009). Cross-linkable copolymers with different functional comonomers are the primary sources of stimuli-responsive membrane. Stimuli-responsive membranes have an extensive application of drug controlled release and sensors/actuators for different stimuli (temperature, light, thermal, pH, etc.) (Qiu and Park 2012). Furthermore, another decided advantage of cross-linkable copolymer membrane is their exceptional thermal, mechanical, and chemical stability after cross-linking reaction, which provides a solid fundament for practical applications in harsh environment.

An increasing number of novel cross-linkable copolymers will be developed with the progress of polymer chemistry. Therefore, they will have broad application prospects in membrane science and technology.

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Cross-Linked Aromatic Polyamide Membranes

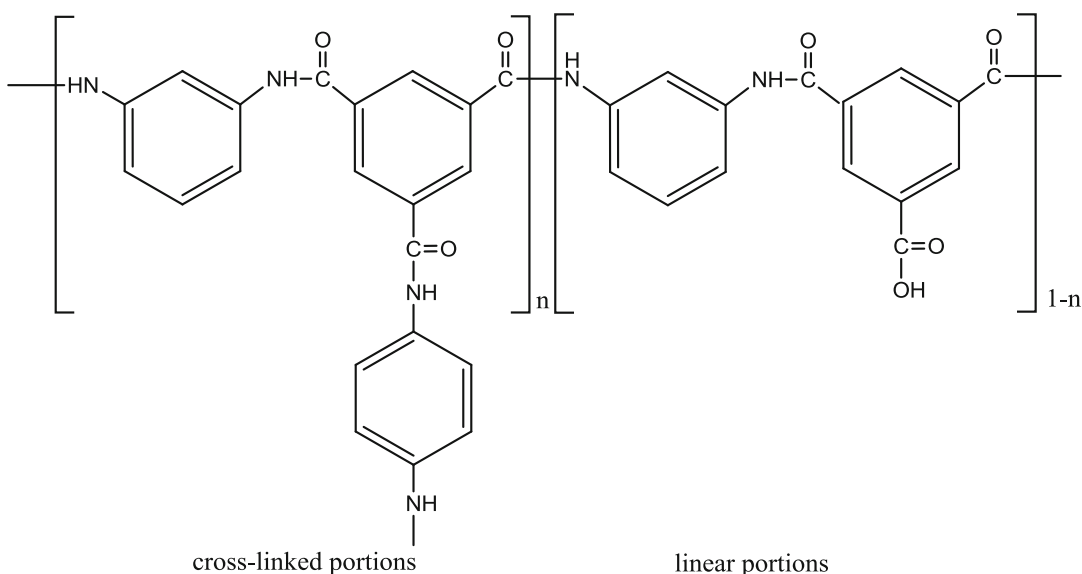
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Cross-linked aromatic polyamide membranes are, typically, the aromatic polyamide-based thin film composite membranes. Aromatic polyamides are macromolecules with repeating units linked by amide bonds, which are produced from the

condensation reaction of the aromatic amino groups and the aromatic carboxylic acid or acid chloride groups (Palmer 2002). Aromatic polyamide fibers, which have high resistance to abrasion, low flammability, and excellent mechanical properties, are widely used in aerospace and military applications. Moreover, aromatic polyamide is also one of the best membrane materials, which can form dense cross-linked aromatic polyamide membranes via interfacial polymerization processes.

The cross-linked polyamide membranes are, usually, used as brackish water or seawater desalination membranes, such as reverse osmosis (RO), forward osmosis (FO), and nanofiltration membranes. Cross-linked aromatic polyamide RO membranes, derived from metaphenylene diamine (MPD) and trimesoyl chloride (TMC), are the most widely used commercial reverse osmosis membranes. The structure of the membrane is shown in Fig. 1. This partially cross-linked chemical structure consists of the cross-linked portions ($C_{18}H_{12}N_3O_3$) and the linear portions ($C_{15}H_{10}N_2O_4$) (Wei et al. 2010). The commercial cross-linked aromatic polyamide RO membranes always exhibit superior water flux and salt rejection, resistance to pressure



Cross-Linked Aromatic Polyamide Membranes, Fig. 1 The barrier layer structure of the cross-linked polyamide RO membrane

compaction, wider operating temperature range and pH range, and higher stability to biological attack, compared with cellulose acetate RO membranes (Li and Wang 2010). Currently, there are kinds of commercial cross-linked polyamide RO membranes, produced by some leading membrane manufacturing companies, such as Dow (Filmtec™), Hydranautics, Toray, GE Osmonics (Desal), and Koch Membrane Systems (Fluid Systems™).

However, the cross-linked aromatic polyamide membranes, including RO, FO, and nanofiltration membranes, have some problems to be solved. The first is the membrane fouling due to its high pollutant deposition tendency (Subramani and Hoek 2010). Membrane fouling, which is a process that the solutes, particles, and bacterium deposit on the membrane surfaces, can cause flux decline and affect the quality of the water produced (Kang and Cao 2012). The second problem is that the chlorine resistance of the membranes needs to be improved compared with cellulose acetate RO membranes (Kang et al. 2007). This is because the amide bonds can be easily halogenated by the free chlorine in the feed solution, resulting in the degradation of the membranes.

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Cross-Linked Layer-by-Layer Membranes

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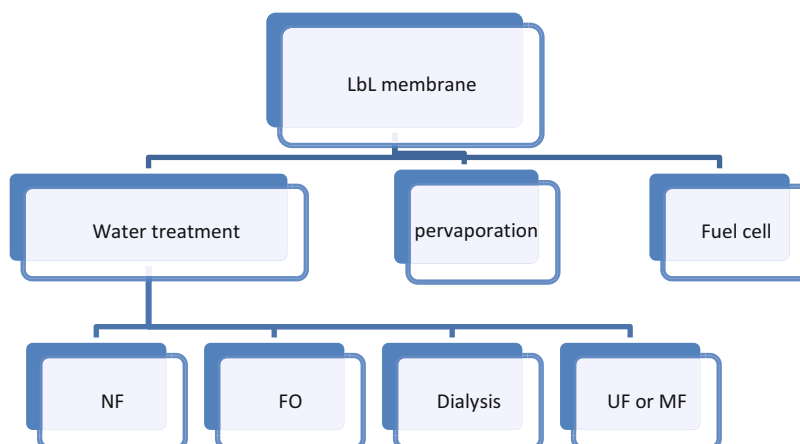
A layer-by-layer (LbL) membrane is formed by coating a porous substrate with polyanions and polycations in an alternative sequence (Decher 1997). Because of the electrostatic forces between the charged polymers, the polyanions and polycations are self-assembled into thin layers. Advantages of LbL membranes include its controllable structure and composition as well as facile process of fabrication and modification. LbL membranes are able to reject a variety of contaminants including divalent ions. Their rejection of monovalent ions tends to be relatively low, but can be potentially improved by posttreatment.

Cross-linking is commonly used to treat LbL membranes for improved rejection and enhanced membrane stability (Qiu et al. 2011). The selective multilayers (the rejection layers) of LbL membrane are mainly formed by the electrostatic interaction that is weaker than covalent bonds. Therefore, the stability of LbL membranes is a key concern in their applications, particularly when the feedwater has high ionic strength that weakens the ionic bonds. The cross-linking treatment offers an effective solution to this problem. The commonly used cross-linking method includes chemical cross-linking (with the help of cross-linking agents such as terephthalaldehyde and glutaraldehyde) (Qi et al. 2012), UV-assisted cross-linking (Duong et al. 2013), and heat-induced cross-linking (Dai et al. 2001). The resultant cross-linked LbL membranes exhibit improved rejection, good chemical resistance, mechanical strength, and long-term stability.

LbL membranes can be classified according to their applications. The common application fields include water treatment (Bruening et al. 2008),

Cross-Linked Layer-by-Layer Membranes,

Fig. 1 Schematic diagram of applications for LbL membrane (Note: *NF* nanofiltration, *FO* forward osmosis, *UF* ultrafiltration, *MF* microfiltration)



pervaporation (Zhao et al. 2011), and fuel cell (Zhang and Shen 2012) (Fig. 1). In water treatment process, LbL membranes present high water permeability and relatively good salt rejection. It is because ultrathin multilayers can achieve high water permeability and dense multilayers can maintain membrane selectivity. On the other hand, LbL membranes usually bring charges that may enhance the rejection due to Donnan exclusion. Additionally, due to the availability of functional groups in polyelectrolyte molecules, LbL method is easily incorporated with other technologies to produce new functional membrane. For example, Ag nanoparticles can be incorporated into LbL FO membrane to produce a novel FO membrane for antibacterials (Liu et al. 2013). In pervaporation, LbL membranes used can produce high permeate flux due to its ultrathin layers, and the selective layer is resistant to organic solvent. In fuel cell, compared with traditional process of fabrication (i.e., spraying, painting, ink-jet printing, and so on), more efficient process could be achieved by using LbL membrane for proton transfer. Additionally, while incorporated with other materials, LbL membranes can increase the catalyst utilization rate so as to enhance the fuel cell performance.

Cross-References

► [Layer-by-Layer \(LBL\) Method](#)

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Cross-Linked Poly(ethylene oxide) Membranes

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Poly(ethylene oxide) (PEO) and its containing polymers have been extensively explored as membrane materials for CO₂ removal from the mixtures with light gases such as hydrogen, nitrogen, and methane (Blume and Pinnau 1990; Li et al. 1995; Okamoto et al. 1995; Bondar et al. 1999, 2000; Hirayama et al. 1999; Yoshino et al. 2000; Kim et al. 2001; Patel et al. 2003, 2004; Lin and Freeman 2004, 2005; Metz et al. 2004; Lin et al. 2006a, b, c; Car et al. 2008; Reijerkerk et al. 2010; Yave et al. 2010; Lau et al. 2011; Liu et al. 2013). The polar ether oxygen has strong affinity with CO₂ with quadrupole moment, but not with light gases, thus providing high CO₂ solubility and high solubility selectivity of CO₂/light gas (Okamoto et al. 1995; Bondar et al. 1999; Lin and Freeman 2004). On the other hand, unlike any other polar groups which would inevitably increase the chain rigidity of the polymer and decrease CO₂ diffusivity and permeability, ether oxygens appear to be the only well-known groups which improve CO₂ diffusivity and permeability (Lin and Freeman 2005; Lin et al. 2006c). Ethylene oxide units have a high concentration of ether oxygens, which makes the ideal as building blocks for membrane materials for CO₂/light gas separation. However, PEO has high crystallinity which is deleterious for gas permeability (Lin and Freeman 2005).

Cross-linking is an effective way to inhibit polymer chain crystallization (Hirayama et al. 1999). Graham proposed empirically that significant crystallinity in cross-linked PEO is not evident when the molecular weight between cross-links is lower than 1,500 (Graham 1987). Cross-linking can be achieved by radiation or radical cross-linking of high molecular weight

PEO or by reactions of end groups such as hydroxyl or vinyl groups. Hirayama et al. prepared cross-linked PEO from mixtures of poly(ethylene glycol) methacrylate (a monomer containing nine EO units) and poly(ethylene glycol) dimethacrylate (a cross-linker containing 14 EO units) by plasma irradiation (Hirayama et al. 1999). They reported that CO₂ permeability increases as monomer content increases while CO₂/N₂ selectivity remains almost unchanged. They prepared a polymer containing 70 wt% monomer; it exhibited a CO₂ permeability of 260 Barrers and a CO₂/N₂ selectivity of about 48 at 35 °C and 1 atm (Hirayama et al. 1999).

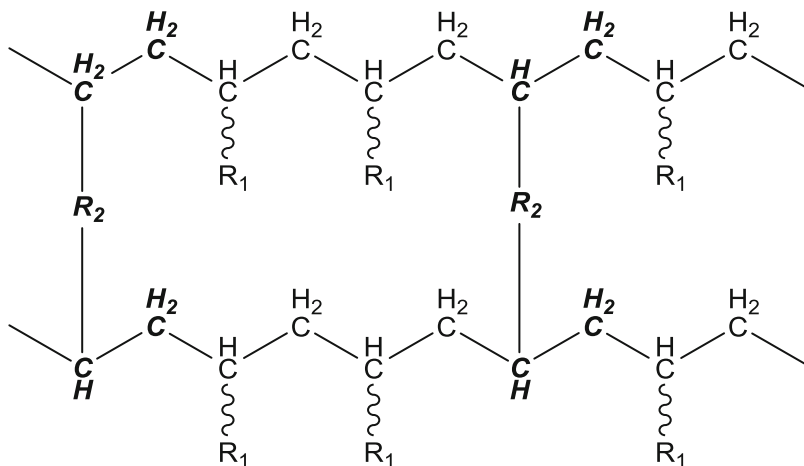
Several series of cross-linked PEO have been prepared by UV photopolymerization of poly(ethylene glycol) diacrylate (PEGDA) containing 14 EO units and poly(ethylene glycol) methyl ether acrylate (PEGMEA) containing about 8.5 EO units (Lin and Freeman 2005; Lin et al. 2006a, c). The resulting chemical structure is shown in Fig. 1 (Kalakkunnath et al. 2005, 2006). PEO crystallinity was completely absent in these copolymers at temperatures as low as −90 °C (the lowest limit of the calorimeter used) due, presumably, to the short nature of the EO branches in the side chains of these materials and to the frustration of crystallization by cross-linking. The average number of EO units per acrylate group is approximately seven, which is the minimum number of monomers required for the unit cell of a PEO crystal (Brandrup et al. 1999). Therefore, using these starting materials, network polymers can be prepared which are noncrystalline and have a high concentration of EO units. The use of acrylate groups instead of methacrylate groups provides higher chain flexibility (or lower glass transition temperature), which can increase gas diffusion coefficients and, in turn, permeability (van Amerongen 1964; Lin et al. 2005).

The inclusion of methyl ether chain end groups in the monomer (as opposed to hydroxyl end groups) increases free volume and improves CO₂/H₂ separation performance of copolymers of PEGMEA and PEGDA. As PEGMEA monomer content increases from zero to 99 wt%, CO₂

Cross-Linked Poly(ethylene oxide)

Membranes,

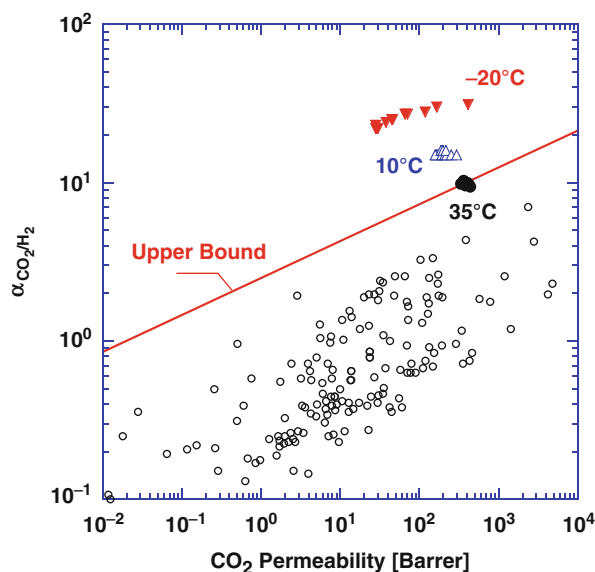
Fig. 1 Schematic representation of PEGDA/PEGMEA copolymer network (Kalakkunnath et al. 2005, 2006). Italicized and bolded parts of the network derive from the cross-linker. R1 is CO (OCH₂CH₂)₈OCH₃ from PEGMEA; R2 is COO (CH₂CH₂O)₁₄OC from PEGDA



Cross-Linked Poly(ethylene oxide)

Membranes,

Fig. 2 Comparison of cross-linked poly(ethylene oxide) membrane with other polymeric membranes in the literature used for CO₂/H₂ separation (Lin et al. 2006a)



permeability increases about fourfold, reaching 570 Barrers, and CO₂/H₂ selectivity increases by 50 %, up to 12, at 35 °C and infinite dilution (Lin et al. 2006). These materials show good CO₂/H₂ separation properties, as shown in Fig. 2. If the -OCH₃ end groups are replaced by -OH end groups, CO₂ permeability and CO₂/H₂ selectivity remain unchanged as the -OH end group content changes across the entire composition window (Lin et al. 2006c).

In general, the cross-linked network materials formed from PEG acrylates and diacrylates provide advantages for CO₂/light gas separation

performance, compared with other PEG-containing polymers such as block copolymers (Lin and Freeman 2006).

1. Cross-linking ensures good chemical resistance, simply because cross-linked networks are not soluble. It is straightforward to incorporate more than 80 wt% PEO in cross-linked polymers from acrylate monomers and/or cross-linkers, which is higher than the maximum value (about 60 %) reported for block copolymers and blends (Okamoto et al. 1995; Yoshino et al. 2000).

2. Cross-linked PEO can be further modified to give much higher CO₂ permeability and CO₂/H₂ selectivity than block copolymers or blends by introducing methyl ether chain end groups (Hirayama et al. 1999; Lin et al. 2006a, c).
3. Finally, cross-linking could completely suppress crystallization at all temperatures of practical interest (Lin et al. 2006c), while block copolymers or blends would still exhibit a melting temperature at temperatures near ambient (Bondar et al. 1999). Consequently, with the cross-linked PEO materials, temperature can be lowered to optimize CO₂ separation performance because lower temperatures favor CO₂/light gas solubility selectivity (Lin et al. 2006a, c).

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Cross-Linked Polyamide Membranes

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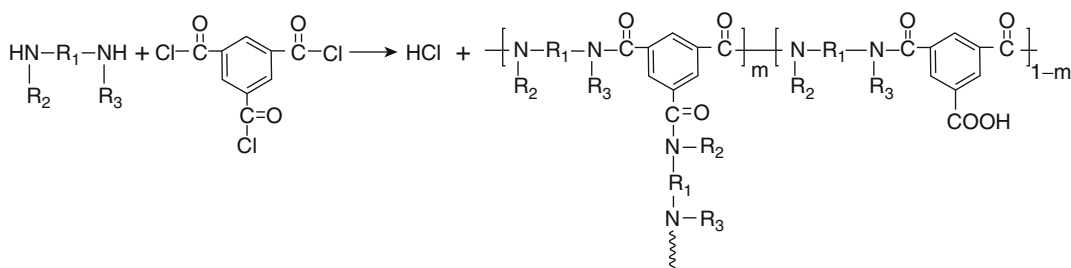
The cross-linked polyamide membrane is one of the most commonly used polymeric membranes for nanofiltration (NF), reverse osmosis (RO), forward osmosis (FO), pervaporation (PV), and gas separation (GS).

The polyamide could be produced either naturally or artificially. The natural polyamides include proteins and peptides. The artificial polyamides, such as nylons and aramids, could be produced by polymerization. Polyamides are widely used in textiles, automobiles, and carpet due to their extreme durability and strength. Moreover, polyamides possess excellent separation property and are promising materials for separation membranes.

The cross-linked polyamide membrane is usually thin-film composite (TFC) membrane consisting of a dense top layer of cross-linked polyamide with a thickness of 0.1–0.3 μm supported by a sublayer with a thickness of 50–150 μm . The membrane is generally fabricated by interfacial polymerization (IP) of di- or multi-amines in aqueous phase and di- or multi-acyl chloride in organic phase on the sublayer. Various diamines have been used to fabricate

membranes for different applications, for example, piperazine (PIP) for NF; m-phenylenediamine (MPD) for RO, FO, and PV; and 3,3'-diamino-N-methyldipropylamine (DNMDAm) for GS (Petersen 1993; Chapman et al. 2008; Lau et al. 2012; Zhao et al. 2012; Li et al. 2012). Trimesoyl chloride (TMC) is the most widely used acyl chloride in IP. The three reactive acyl chloride groups of TMC could form the cross-linked structure that potentially enhances both separation performance and mechanical strength of the membrane. The reaction between these two reactive monomers, i.e., diamine and TMC, is shown in Fig. 1. The formed polyamide contains both cross-linked structure and linear structure. The linear structure is caused by the hydrolysis of acyl chloride group. The ratio of cross-linked part to linear part of the polyamide, as well as the surface characteristic and the thickness of polyamide layer, could be finely adjusted by changing technological parameters of IP process, such as solvent type, monomer concentrations, reaction time, and posttreatment conditions. The performance of the membrane therefore could be improved by optimizing the structures.

The cross-linked polyamide membranes for NF and RO in applications of desalination have been successfully commercialized for decades. There are several membrane suppliers providing NF and RO membranes for large-scale desalination plants, such as DOW, Toray, Hydranautics, and Toyobo. The salt rejection and water permeability of NF and RO membranes have been drastically improved during these years but the



Cross-Linked Polyamide Membranes, Fig. 1 Reaction scheme for preparation of cross-linked polyamide membranes by IP

antifouling and chlorine resistant properties of the membranes still have to be enhanced (Xu et al. 2013). The cross-linked polyamide membranes for FO in applications of desalination are still in laboratory research due to the challenges of concentration polarization, fouling, and reverse solute diffusion (Zhao et al. 2012). The cross-linked polyamide membranes for PV in applications of dehydration and for GS in applications of CO₂ separation are fabricated in laboratory scale at present, because the permeance and selectivity of membranes have to be improved to fulfill technical and economical requirements of practical applications. The improvement of separation performance of membranes for GS could be achieved by combining multiple separation mechanisms into a single membrane through selecting proper monomers in IP process (Li et al. 2012).

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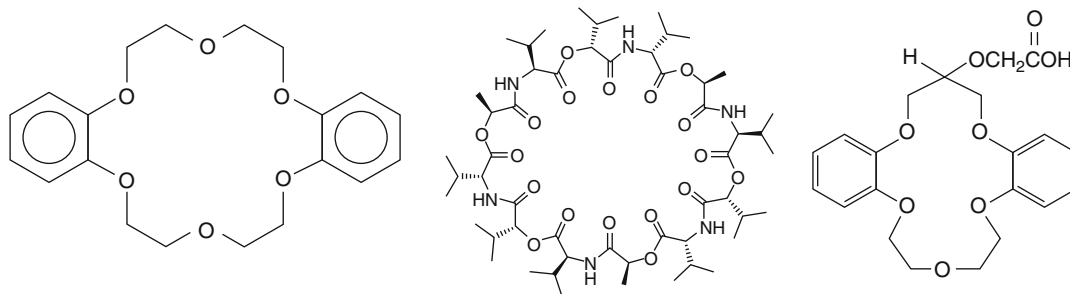
Crown Ethers

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Pedersen (1967) synthesized the crown ethers (see Fig. 1a) for the first time in 1967 which formed

stable complexes with alkali/alkaline earth metal ions and displayed a unique selectivity based on the size compatibility of the ligand cavity size and the ionic size of these metal ions. The crown ethers mimic the biological receptors such as valinomycin (see Fig. 1b) which selectively transports K⁺ ion as compared to Na⁺ ion (by a factor of 10⁵) across cell membranes. The transport properties of the crown ethers depend on the size of the crown ring, number of donor atoms, nature of donor atoms, nature of lipophilic/ionizable side arms, etc. Crown ethers have been overwhelmingly used for the transport of alkali metal/alkaline earth ions, though there have been quite a large number of reports on the transport of Ag⁺, Hg²⁺ (with thia-crown ethers), and Pb²⁺ which are proposed for heavy metal removal from wastewaters (Lamb et al. 1980). There have also been several reports on the use of crown ethers for the selective transport of lanthanides and actinides though size selective factors are far less pronounced in such cases. Another major application of crown ethers for metal ion transport includes the recovery of radio-caesium and radio-strontium from radioactive wastes which can significantly reduce the load on the vitrified glass blocks (Dozol et al. 1995; Dozol and Casas 1994). Crown ether-based supported liquid membranes have shown large amounts of acid cotransport when attempts have been made for the transport of Cs-137 and Sr-90 from nitric acid feeds. This has affected the overall efficiency of the transport process, and appropriate selection of the diluent has helped in overcoming this issue (Raut et al. 2012). Though crown ethers have been employed for the transport of Cs(I) in laboratory-scale studies, calix crowns (where crown ether structure has been appended to a calix[4]arene) have been proposed as one of the most efficient carrier extractants for the effective transport of radio-caesium (Casnati et al. 1995). Transport of organic/biological receptors like cytochrome C (Paul et al. 2003) and amino acids (Yamaguchi et al. 1988) has also been facilitated by crown ethers.

Usually, the neutral macrocyclic ionophores like crown ether, cryptand, calixarenes, cavitands, etc. require a large lipophilic counter anion like



Crown Ethers, Fig. 1 Structural formulae of (a) a typical crown ether, (b) valinomycin, and (c) an ionizable lariat crown ether

picrate, tetraphenyl borate, etc. for the effective transport of the cationic species from the aqueous phase to the membrane phase. The ion pairs are subsequently transported across the membrane phase which usually contains a polar diluent such as chloroform, long-chain alcohols, ethers, etc. for the stabilization of the charged metal-carrier (crown ether) complex. However, the large molar volume counter anions can make the diffusion of the ion pair rather slow. Appending an ionizable pendent arm to the crown ether ring (the ligand is called an ionizable lariat ether; see Fig. 1c) can eliminate the need for the counter anions making it a more efficient transport system (Strzelbicki et al. 1989). Other types of functionalization have been found to impart exotic properties to the receptors. For example, crown ethers with suitable functional groups based on redox-switched (Shinkai et al. 1985a), thermosensitive (Shinkai et al. 1985b), and photoresponsive (Shinkai et al. 1981) properties have also been used for the transport of receptors. Functionalized crown ether-type ligands with carboxylate groups have been suggested for the recovery of U from seawater which is yet another exotic application of the crown ether-based membrane transport systems.

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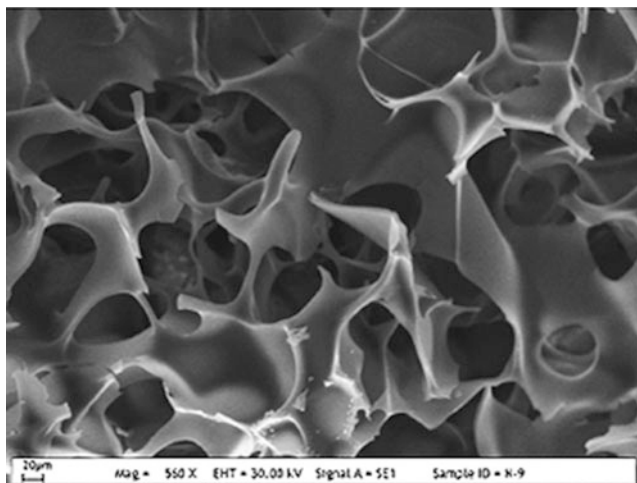
Cryogels

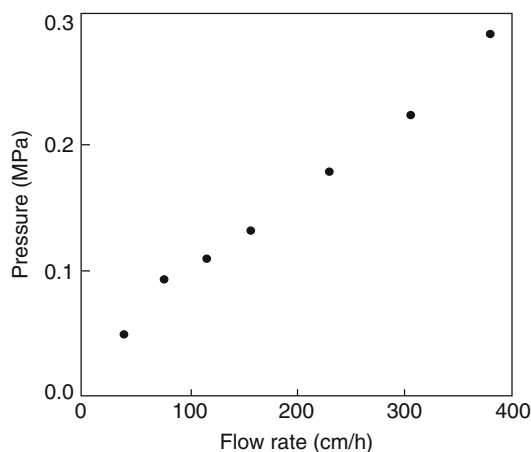
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Chromatography is the most powerful technology in the downstream applications for the separation of proteins both in the analytical and large scale. Conventional packed bed columns have been used for many applications; however, they have some important drawbacks such as the slow diffusional mass transfer and the large void volume between the beads (Gun'ko et al. 2013). In order to resolve these problems, nonporous beads and perfusion chromatography packing have been designed and used as a carrier, but these adsorbents are not sufficient to resolve these limitations in essence. New-generation stationary phases i.e.,

polymeric cryogels, are found to have an increasing use in the separation science due to their easy preparations, excellent flow properties, and high performances compared with the conventional beads. Cryogels are mega-porous three-dimensional networks formed under freezing conditions. The pore size of the cryogels varies from 10 to 250 μm (Fig. 1), which can be changed by optimizing the freezing regime and type and concentrations of polymerization precursors. The unique properties of cryogels like osmotic, chemical, and mechanical stability, large pores, short diffusion path, low-pressure drop (Fig. 2), and short residence time for both binding and elution stages make them attractive matrices for affinity chromatography of large molecules such as proteins, plasmids even whole cells, as well as small molecules (Lozinsky et al. 2001; Stela and Valentina 2013; Bereli et al. 2008, 2010; Tamahkar et al. 2011; Derazshamshir et al. 2010). Therefore, cryogels can be used in the various affinity chromatography applications such as protein A affinity chromatography, histidine affinity chromatography, thiophilic affinity chromatography, metal-chelate affinity chromatography, dye affinity chromatography, ion-exchange chromatography, DNA affinity chromatography, cell affinity chromatography, molecular imprinting technique, etc.

Cryogels, Fig. 1 SEM images of the PHEMA cryogel





Cryogels, Fig. 2 Pressure drop at different flow rates

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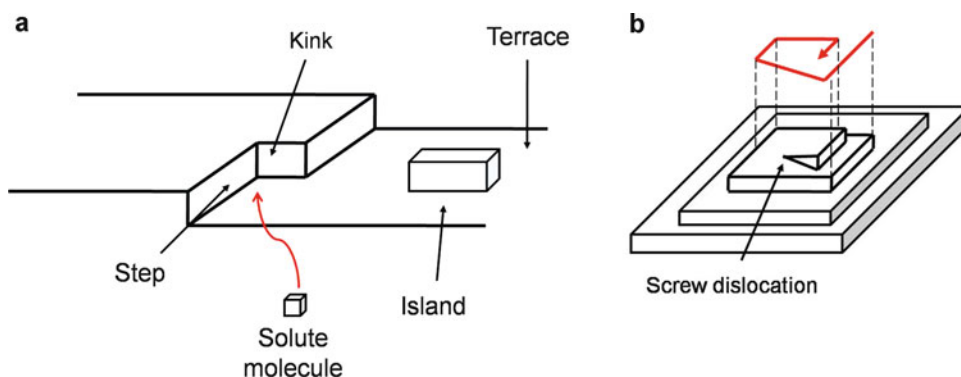
Crystal Grow

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Crystal growth is the second stage of the crystallization process and consists in the addition of

new atoms, ions, molecules, or polymer strings on preformed crystalline nuclei coming from the nucleation stage. The result of the crystal growth is the formation of a crystalline solid, whose atoms are reciprocally fixed in the space according to the symmetry rules characteristic of the space group in which the growth takes place. Similarly to crystal nucleation, crystal growth requires that the concentration of the solute is in the supersaturation range (metastable zone): when supersaturation is reached, the number of molecules that attach the crystal surface exceeds that of the molecules that detach, leading to an increase of crystal dimension. The strength of bonding formed between the crystal surface and the new molecules depends on the temperature rather than the concentration of the solute. Accordingly, crystal growth requires a lower supersaturation level than that required for nucleation stage; however, too low supersaturation can result in the crystal dissolution. Traditionally, crystal growth is divided in two distinct phases: (a) transfer of mass from the crystallizing solution to the crystal/solution interface, which is governed by diffusion and convection mechanisms, and (b) the attachment of molecules on the preformed crystal. Crystal surface consists of flat regions (terraces), raised layers (steps), islands, and kinks (Fig. 1a), each having different abilities to interact with new molecules from the bulk of the solution. Differently from the flat surfaces, kinks are the most suitable sites to promote crystal growth, since the presence of adjacent walls to which new molecules can attach allows reducing the activation energy to incorporate new molecules (Chernov 1984). In the presence of high density of kinks, crystal growth occurs in spiral fashion around the single kinks and expands by rotating around the emergence of the screw dislocation (screw dislocation mechanism) (Fig. 1b). Differently, in the case of crystals with perfectly flat faces, the molecules coming from solution tend to form two-dimensional layers on the surface due to the lack of suitable attachment points to bind the crystal surface. The mechanism is slow and requires high supersaturation. In both cases, the increase of crystal dimension stops when the density of impurities on the surface of the crystal



Crystal Grow, Fig. 1 Crystal growth process. (a) The molecule of solute binds to the kink site after adsorbing and diffusing across the terraces. (b) Geometry of a screw dislocation. The existence of a critical size leads to the

formation of the spiral structure (growth direction in *red line*), since the new segment of the step cannot move until it reaches that size

reaches a critical value able to poison the process (Durbin and Feher 1990). Quality of the crystals strictly depends on the supersaturation level and, hence, on the ratio between the rate of nucleation and crystal growth: while a low level of supersaturation favors the crystal growth and slowly leads to few large crystals usually having high quality (Frank 1949), higher supersaturation supports an excess of nucleation and leads to a rain of small crystals. The use of membranes as dosing devices to modulate the solvent removal from the crystallizing solution by varying process parameters and membrane features makes possible the control of the extent both of nucleation and of crystal growth: variations able to increase the supersaturation stimulate the nucleation at the expenses of crystal growth, while variations influencing the transmembrane flux can slow the achieving of the supersaturation, encouraging the crystal growth over nucleation. It follows that crystals appear after more time, but they are larger and usually of high quality (Curcio et al. 2003; Zhang et al. 2008). In addition, the use of membrane devices as active supports of crystallization allows to induce the nucleation and crystal growth stages in separate sites. This reduces the risk of membrane fouling, even when the same membrane supports heterogeneous nucleation, and allows to fully exploit the advantages coming from heterogeneous nucleation and growth at low supersaturation, leading to a great production of large crystals.

Cross-References

► [Crystal Nucleation](#)

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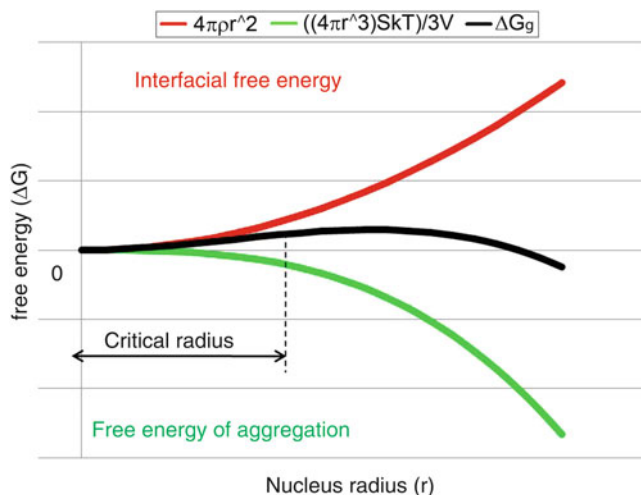
Crystal Nucleation

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Crystal nucleation is the first stage of a crystallization process and leads to the formation of distinct crystal nuclei. It is a local phenomenon of aggregation, and it is said to be homogeneous when it occurs in the bulk of the solution and

Crystal Nucleation,

Fig. 1 Effect of the nucleus radius (r) on the free energy of germination ΔG_g (in black color). Interfacial free energy and free energy of aggregation are reported in red and green color, respectively



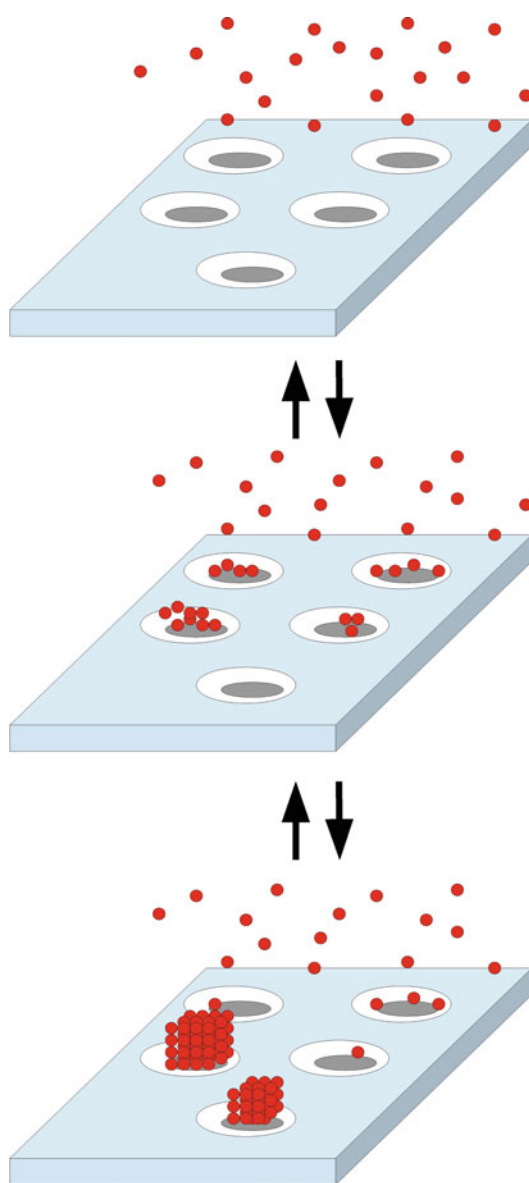
heterogeneous on very small solid particles, such as amorphous clusters or crystalline particles. In both cases, the formation of crystal nuclei requires well-oriented collisions between molecules to occur. The activation energy necessary to induce nucleation is represented by the free energy of germination $\Delta(G_g)$ shown in Eq. 1 (Mullin 1972), consisting of a positive term called interfacial free energy (in red color in Fig. 1) and a negative term called free energy of aggregation (in green color in Fig. 1):

$$\Delta G_g = 4\pi\rho r^2 - ((4\pi r^3)SkT)/3V \quad (1)$$

In the Eq. 1, V is the volume of the molecule to crystallize, ρ is the interfacial free energy, T is the temperature, k is the Boltzmann factor, and r is the average radius of the crystal nuclei. ΔG_g reaches a maximum value for a given nucleus radius (Fig. 1); therefore, only crystal nuclei that grow up to this dimension are stable, while smaller nuclei dissolve before to pass the next crystal growth. In order to reduce the energy of activation, high S value, that is an estimation of the supersaturation level of the solution, is required. Supersaturation is an essential condition required during each stage of the crystallization process; however, the nucleation, being the most energy expensive stage of the entire crystallization process, requires higher supersaturation level to take

place. The mechanism and the rate of nucleation strongly influence quality and quantity of the produced crystals; therefore, many efforts are devoted to control the nucleation in order to obtain crystals having high quality. One of the main problems in industrial or laboratory crystallization processes is the excess of nucleation that usually leads to a rain of tiny poor-quality crystals. The use of filtered solutions is the solution commonly adopted to overcome this problem; however, in the cases where nucleation is welcome, the presence of dust or small foreign particles, such as mica or silica able to promote heterogeneous nucleation, can represent an advantage (Falini et al. 2002; Saridakis and Chayen 2009). These particles, also called crystallization seeds, act as nucleant and usually increase the chances of crystallization by facilitating the proper molecular orientation during the formation of the crystal nuclei (Bolanos-Garcia and Chayen 2009). The result is the reduction of the activation energy and, consequently, the decrease of the supersaturation level required to induce the formation of crystal nuclei with respect to that required in the homogeneous nucleation. In these conditions, nucleation could even occur in the metastable zone where crystals grow larger and better ordered than those grown at higher supersaturation level. The direct contact between crystallizing solution and an irregular surface can induce heterogeneous

nucleation, as occurs in membrane crystallizers (Di Profio et al. 2003, 2005). The local entrapping of the solute molecules in the pores of the membrane causes an increase of the local level of supersaturation (Curcio et al. 2006), inducing the



Crystal Nucleation, Fig. 2 Mechanism of crystal nucleation on membrane. Solute molecules (*red spheres*) are adsorbed on the surface and are trapped inside the pores of the membrane, resulting in an increase of local concentration

formation of crystal nuclei also in the presence of lower amount of initial substance. For this reason, membrane crystallizers are particularly attractive for crystallization processes where the solute is expensive, such as in the case of proteins. In addition, a fine regulation of the nucleation rate can be achieved by managing the transmembrane flux of the solvent from the crystallizing solution toward the stripping solution located on the other side of the membrane. Nucleation mechanism on the membrane (Fig. 2) consists of a first phase where solute molecules are adsorbed on the surface by means of attractive interactions able to properly orient the molecule and that usually drive the growth of the crystal toward a specific crystal structure (Di Profio et al. 2009). The effective control of the nucleation process by means of an appropriate choice of the porosity and hydrophobicity of the membrane and by managing the transmembrane flux makes membrane crystallizers particularly suitable for industrial applications.

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Crystal Polymorphism

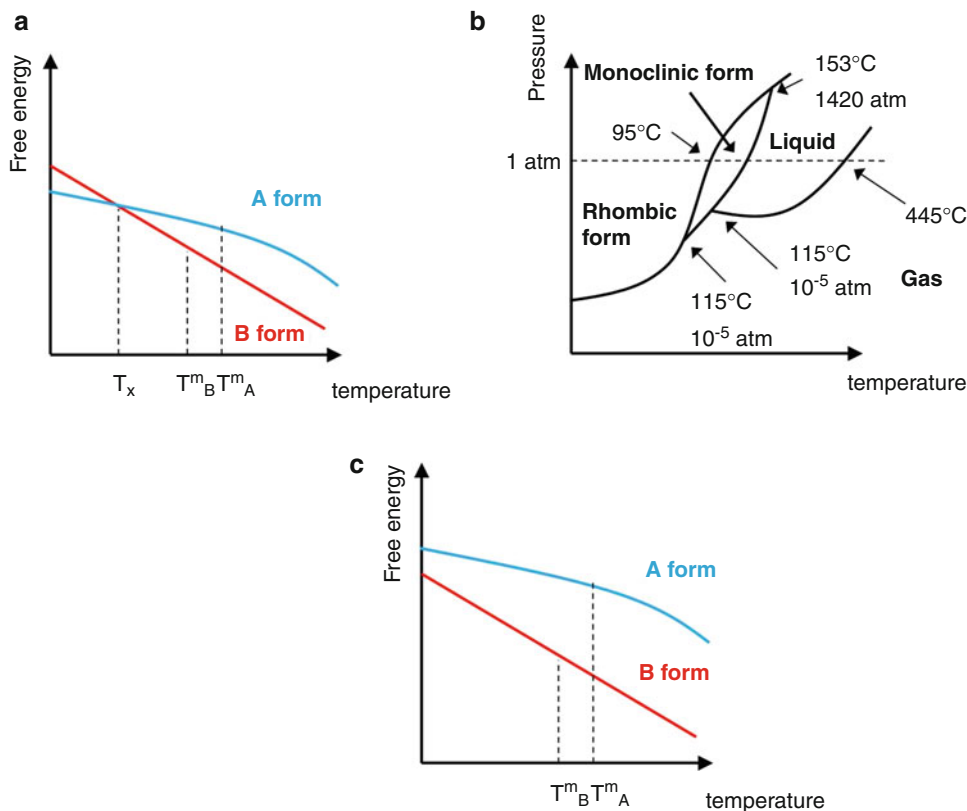
Polymorphism

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The term polymorphism comes from the Greek word *polus* = many and *morph* = shape, and it is the propriety of the chemical substances to exist in more crystal forms, each having a specific arrangement of atoms or ions in the crystal lattice. Crystal polymorphism includes the allotropy

phenomenon, which refers to pure elements. Crystal forms that differ for packing or for molecular conformation are said packing or conformational polymorphs, respectively. From a thermodynamic viewpoint, polymorphism can be of two kinds: enantiotropic (Fig. 1a), in the case of crystal forms stable in a precise range of temperature and pressure (e.g., the system rhombic sulfur-monoclinic sulfur in Fig. 1b), and monotropic (Fig. 1c), in the case of crystallization process that spontaneously evolves toward a crystal form characterized by lower internal energy with respect to the other forms (metastable forms). Generally, monotropes and enantiotropes can be recognized by their heats of fusion, since monotropes come from exothermic processes and



Crystal Polymorphism, Fig. 1 Enantiotropic and monotropic systems. (a) Variation of free energy with temperature for enantiotropic substances. The temperature T_x , which marks the boundary between stability zones for A and B forms, is below the melting temperatures of the two substances (T_A^m and T_B^m). (b) Phase diagram for the

enantiotropic system rhombic sulfur-monoclinic sulfur. (c) Variation of free energy with temperature for enantiotropic substances. No crossing of free energy curves belonging to the A and B forms can be observed below of their melting temperatures (T_A^m and T_B^m)

enantiotropes from endothermic processes. Whatever is the kind of polymorphism, under static crystallization conditions, the probability of carrying out crystallization precisely at the boundary that separates the polymorphic forms is small; therefore only one crystal form appears at the end of the crystal growth. The mechanism that explains the polymorphism involves the stage of crystal nuclei formation. During the nucleation stage, some molecules can leave the preformed aggregates, leading to their complete dissolution. The surviving aggregates provide the new differently arranged templates for the subsequent growth stage, and the molecular arrangement in largest amount will form the nuclei that will grow in a particular crystal form. The critical dimension that the aggregates must reach to survive depends of the supersaturation level; therefore, the entire process is under kinetic control rather than thermodynamic (Volmer 1939; Ostwald 1987). Today, the interest for the phenomenon of polymorphism is increasing, particularly for pharmaceutical industry where its study is became integral part of the drug optimization process (Brittain 1999). Paracetamol (Beyer et al. 2001), famotidine (Lu et al. 2007), and piroxicam (Giordano et al. 1998) are the classical examples of drugs crystallized in several forms, each having different chemical and pharmaceutical proprieties. Usually, pharmaceutical industry prefers the most stable form with respect to that metastable, although, at the same concentration, the latter is more available in the organism due to its higher solubility. Also protein molecules can crystallize in several crystal forms, as a consequence of the different conformations assumed by peptide chain in a given condition. A classic example of polymorphism for crystal of proteins is the lysozyme that crystallizes in six different crystalline forms. Another important example is the ubiquitin, whose crystal form depends on the nature and the amount of the metal ion used during the crystallization (Arnesano et al. 2011; Falini et al. 2009). The technology of membrane crystallizers gives the opportunity to drive the crystallization toward a specific polymorph. This is possible by regulating the degree and the rate to which of supersaturation is reached through the

managing of the transmembrane flux and an accurate choose of the membrane properties (Di Profio et al. 2007, 2009, 2013). So crystallization assisted by membrane can occur both under thermodynamic and kinetic control: low evaporation rates through the membrane allow the growth of the more stable nuclei at the expense of the less stable forms (thermodynamic control), while the induction of a more rapid nucleation increases in the presence of higher evaporation rates and increases the conversion rate from the stable to the metastable form (kinetic control). The relative amount of the two forms depends on the ratio between the conversion and crystallization rate. Similarly, the production of a specific polymorph can be obtained by using antisolvent membrane crystallization processes (Di Profio et al. 2010).

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Crystal Purity

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Crystal purity is the parameter used to indicate the contamination level of a crystal and represents one of the most important properties of the crystalline materials. Crystal purity is also an index of the heterogeneity of the substance to crystallize, in particular in the presence of proteins or nucleic acids, whose uncontrolled modifications may increase the number of species in the crystallizing solution. Contaminants may distort the crystal lattice, affect the crystal features, such as diffraction quality, and change the crystal morphology in particular when the impurities are incorporated in the crystal at different rates into adjacent steps on the crystal surface. However, the main feature of a low-purity crystal is its higher internal energy with respect to that in absence of impurities (van Enkevort and van der Berg 1998; Davis et al. 2004), which causes an increase of the crystal solubility and a decrease of the effective supersaturation level of the solution containing the substance to crystallize: the higher the contamination, the more difficult the crystallization because the dissolution probability of the crystals increases. Given this, many efforts should be devoted to adequately purify the substance to crystallize, by paying attention to the purity grade of the chemicals employed in each step. Particular attention should be paid for precipitant agents, since they are used in very high concentrations: accordingly, salts and polymeric precipitants, such as polyethylene glycol or alcohols, should be recrystallized or purified, respectively. Once the crystal is formed, washing procedures

may be carried out to increase crystal purity by removing many of the surface impurities or those specifically attached inside the crystal. However, the technique is quite risky, since the washing solvent should be able to remove the impurities without dissolving the crystal. Although contamination is usually the first cause of unsuccessful crystallization, the alone presence of impurities is not sufficient to frustrate the crystallization attempts. Crystal features, such as crystal lattices having weak interactions between atoms or containing large empty spaces where foreign molecules have possibility to fit, should be avoided to reduce the probability of crystal contamination. Impurities are included in a crystal as a result of the processes that occur concomitantly to the crystallization (in particular during the nucleation) or after that crystal growth has finished. Particularly, the degree of crystal purity depends on the ratio between the rates of these inclusion processes with that of the crystallization process that, being a purification process, pushes toward the recovery of the desired product without contaminations (Burton et al. 1953): usually, slow crystallizations allow the substance to crystallize to properly fit in the lattice, differently from more rapid precipitations, where the insertion of the impurities results facilitate. In addition, high supersaturation often leads to contaminant inclusions that reduce the crystal purity. At the present, membrane technology represents one of more promising tools to produce high-purity crystal. By controlling the transmembrane flux, membrane crystallizer can limit the maximum level of supersaturation and reduce the growth rate to reach the critical threshold, beyond which inclusion of impurities occurs (Weckesser and König 2008; Mullin 1993). Today, the advances made in the development of membrane-assisted crystallization allow producing crystalline materials having the purities required for their commercialization as purified product. One of the most important examples is represented by the production of sodium carbonate crystals having purity grade that reaches ca. 99.5 % also starting from crystallizing solutions containing concentrations ranging from 0.2 to 0.6 M of impurities, such as sodium nitrate, sodium sulfate, and sodium chloride

(Ye et al. 2013). In addition, membrane devices are also used to produce high-purity cocrystal, a challenge particularly interesting for pharmaceutical industry.

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(in g/cm²), and C_f is the sensitivity factor for the crystal used (in Hz.cm².ng⁻¹). This sensitivity is proportional to the square of the resonant frequency, according to the expression

$$C_f = \frac{\Delta f}{\Delta m} = -\frac{2}{\rho v} \frac{f_n^2}{n}$$

where ρ is the quartz density, v is the propagation velocity of the wave in the crystal, f_n is the frequency of the selected harmonic resonant mode, and n is the harmonic number ($n = 1$ for the fundamental mode). By way of comparison, the typical balances used in research labs (torsion, cantilever, or spring balances) are able to detect mass until 10⁻⁷ g, while QCM can detect up to 10⁻¹³ kg (Mecea 2005). For many years QCMs were only applied as gas-phase mass detectors in physical vapor deposition systems. Their application has been extended recently, with other uses beyond mass deposition, including the monitoring of adsorption kinetics for biomolecules and sensors based on QCM detection.

Crystal Quartz Microbalance

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The quartz crystal microbalance (QCM) is a mass sensor able to measure mass below the nanogram scale range. This device was first introduced by Sauerbrey in 1959 (Sauerbrey 1959), and its operation is based on a piezoelectric plate of quartz with two electrodes fixed to the plate. The small mass absorbed at the crystal is detected by decreasing the resonant frequency of the crystal. The Sauerbrey's equation is used to associate the mass adsorbed at the QCM crystal surface with the change in oscillation frequency of the crystal:

$$\Delta f = -C_f \Delta m$$

where Δf is the experimental frequency shift (in Hz), Δm is the change in mass per unit area

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Crystal Quartz Microbalance for Protein Adsorption Measurement

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With the advent of biosensors, techniques able to monitor the immobilization of active molecules on electrodes become essential, especially those able to provide molecular-level information for the adsorption process. Proteins represent an

example of molecules largely used in biosensors, and their immobilization process onto electrode surfaces has been monitored by techniques such as fluorescence labeling (Lee 1997), microarray techniques (Park et al. 2008), surface plasmon resonance (SPR) (Smith et al. 2003), and quartz crystal microbalance (QCM) (Cooper and Singleton 2007). The latter has become the most used because it allows for determining the amount of bound molecules at the electrode surface and evaluation of the adsorption kinetics and of the affinity between ligands and analytes in sensors.

A quartz crystal microbalance (QCM) is a device often used to monitor the material adsorption, being capable to detect mass change of the order of 10^{-9} g in commercial systems. The QCM principle of operation is based on changing the resonance frequency of a quartz crystal by adsorbing mass on its surface (Montagut et al. 2011). For monitoring protein adsorption, usually a ligand is immobilized as a monolayer on a gold surface. Since gold reacts with thiols producing active sites at the surface, proteins can be immobilized by the thiol groups from their cysteine residues or can be activated by using a thiol-containing bifunctional linker (Bieri and Burgi 2006).

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Crystal Seeding

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Synonyms

Seeding

Crystal seeding is a technique widely employed to provide preformed templates (seeds) on which new molecules can converge to form crystals. Crystal seeding is said homogeneous if the seeds are made of the same molecule to crystallize, as occurs in macroseeding, microseeding, and streak seeding, and heterogeneous if it foresees the use of foreign material, such as porous silicon and mica (Saridakis and Chayen 2009), as in the case of cross seeding and epitaxial growth. Whatever the kind of used seeds, their presence generally makes less energetically expensive the entire crystallization process, because it allows the passing directly to the crystal growth stage without dealing with the intrinsic uncertainties of the nucleation. However, the usage of seeds might have the disadvantage to affect the crystal growth and the forming crystal lattice (Hermes et al. 2011; Liu et al. 2007). The first step for much of seeding techniques is the production of seeds: during this phase, preformed crystals are washed to remove defects and impurities that could block the crystal growth, stabilized in an appropriate solution, and crushed by using a glass homogenizer or by using spherical beads. Once the seed stock has been obtained, pre-equilibrium conditions (e.g., temperature, precipitant agents, additives, etc.) of the solution to seed are carefully determined together with the appropriate level of supersaturation, in order to avoid the trigger of a self-nucleation that would frustrate all following efforts. In the absence of such information, the seeding process could result in a dissolving of the seeds or in a rain of tiny and poor-quality crystals. In order to assess seeding conditions, protein crystallographers usually exploit streak seeding

technique, where a synthetic or natural fiber (Bergfors 2003) is used to crush existing crystals and to introduce the resulting small crystalline particles into different pre-equilibrated solutions: mode and timing of seed growth allow to determine both the appropriate range of pre-equilibration conditions and the dilution of the seed stock. Although the techniques of seeding were initially developed with the aim to optimize and make more reproducible the crystallization processes performed in laboratory, today they are widely employed also in high-throughput processes that range from the industrial crystallizations to the preparation of devices employed in membrane reactors or in separation processes, such as membranes of zeolite (Li et al. 2005) or silicate crystals (Hasegawa et al. 2006). Preparation of these membrane devices is very challenging because it requires a strong control of the seeding in order to obtain high-quality membranes having determined features, such as a specific crystalline orientation (Caro et al. 2000). Several seeding techniques have been developed to produce a membrane of zeolite crystal (Table 1), and the secondary growth together with dip coating is considered among those most promising: secondary growth exploits a hydrothermal treatment of the membrane support that has been previously covered with layers of seeds (Lovallo and Tsapatsis 1996), while dip coating takes advantage from the capillary force to aid the deposition of crystal seeds (Lovallo et al. 1998; Bernal et al. 2001). In addition, filtration

procedures, such as cross-flow filtration and dead-end filtration (Pera-Titus et al. 2005; Huang et al. 2004), based on the seed deposition on the membrane support under the action of a difference of pressure applied, have been also developed.

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Crystal Seeding, Table 1 Seeding procedures for zeolite membrane preparation

Seeding procedure	References
Secondary growth	Lovallo and Tsapatsis (1996)
Dip coating	(Lovallo et al. 1998; Bernal et al. 2001)
Spin coating	Mintova and Bein (2001)
Rubbing	(Kusakabe et al. 1998; Hasegawa et al. 2002)
Cationic polymer use	(Hedlund et al. 1999; Weh et al. 2002)
Cross-flow filtration	Pera-Titus et al. (2005)
Dead-end filtration (vacuum seeding)	Huang et al. (2004)

- Pera-Titus M, Llorens J, Cunill F, Mallada R, Santamaria J (2005) Preparation of zeolite NaA membranes on the inner side of tubular supports by means of a controlled seeding technique. *Catal Today* 104:281–287
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Crystallization

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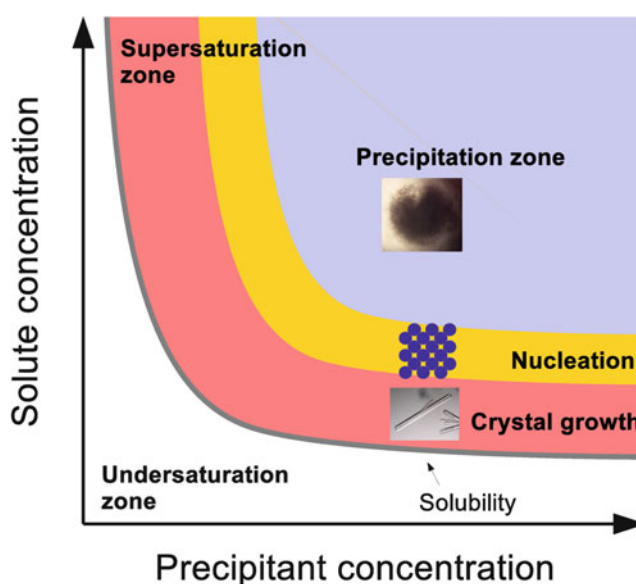
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Crystallization is a phase transition that takes place from the liquid toward the solid state resulting in the formation of crystals; less frequently, the deposition of crystals can also occur starting from the gas state. In any case, crystallization process represents a particular kind of solidification in which the molecules or ions of a given substance arrange themselves in an orderly fashion according to a substance-specific

three-dimensional lattice. Differently, in the absence of orderly arrangement, solidification process leads to amorphous precipitates or to solids consisting of a mix of crystalline and amorphous areas (as it happens for some polymers). Crystallization takes place when the solution containing the substance to crystallize reaches the supersaturation state, namely, when the concentration of this substance overcomes the solubility limit while remaining below the threshold of precipitation. The kinetics and the thermodynamics of the crystallization depend on the supersaturation level that, hence, represents the driving force of the entire process. Crystallization consists of two major events: nucleation and crystal growth. Nucleation occurs in the metastable zone (Fig. 1, in yellow) as a consequence of the rapid local molecular collisions characterizing the homogeneous phase (solution or gas) in condition of supersaturation. Crystalline nuclei, the smallest molecular aggregates having a structure ordered according to periodic rules, can be formed only when well-oriented collisions between particles take place. The smallest nuclei dissolve, while crystal nuclei having critical dimensions pass to the next step, where other molecules of solute can converge on the preformed aggregates. This stage is called crystal growth and takes place in the

Crystallization,

Fig. 1 Crystallization phase diagram. Crystal nucleation takes place in metastable zone (in yellow) and crystals growth in labile zone (in pink), both belonging to the supersaturation zone. The condition of supersaturation is reached when solute concentration is slightly higher than the solubility (gray line); differently, a much higher solute concentration leads to amorphous precipitation (light cyan area)



labile zone (Fig. 1, in pink). During the crystal accretion, also the concentration of contaminants on crystal surface increases causing a slowdown of the growth up to its complete stop. The adding of small particles, such as small crystals or amorphous solids (Saridakis and Chayen 2009), can promote the crystallization process by acting as nucleation centers. Although the rates of nucleation and crystal growth increase with the supersaturation level, fast crystallization processes at low supersaturation are possible in the presence of crystal defects. Today, advanced crystallization techniques allow getting crystals with few defects even starting from lower levels of supersaturation. This is possible by means of an effective control of the nucleation and crystal growth steps, as occurs in the case of the membrane-assisted crystallization (Drioli et al. 2012), where the entire crystallization process takes place on a support consisting of a polymeric membrane that acts also as active surface for heterogeneous nucleation (Di Profio et al. 2010a). On the other side of the membrane (distillate side), a stripping solution allows the removal of the solvent from the crystallizing solution. The high hydrophobicity of the membrane prevents its wetting, allowing that the mass transfer between crystallizing solution and stripping solution takes place only by vapor diffusion mechanism. Since the solute species, such as macromolecules and electrolytes, have lower volatility than the solvent, only the latter passes from the crystallizing solution to the stripping solution through the membrane, by resulting in an increase of solute concentration. Therefore, the driving force of the membrane-assisted crystallization is represented by the vapor pressure gradient at both sides of the membrane. Kinetics and thermodynamics of the nucleation process can be modulated according to the transmembrane flux and the features of the membrane, offering the opportunity of a more rationale design of the crystallization process. Crystallization on membrane has been extensively tested both on small molecules (Di Profio et al. 2010b, 2013) and on large macromolecules, such as proteins (Di Profio et al. 2005; Curcio et al. 2005).

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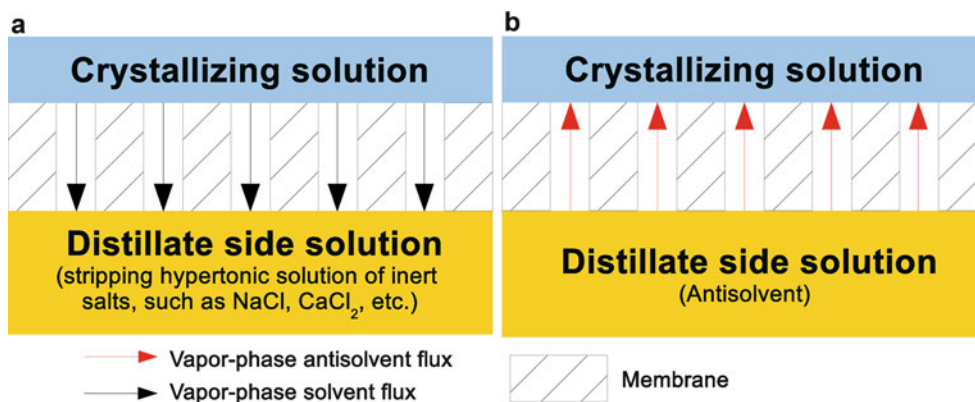
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Crystallizing Solution

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Crystallizing solution (also called crystallizing cocktail) is the ensemble of chemicals able to promote the crystallization of a substance in a given physical condition (e.g., temperature, vibrations, surface of crystallization, etc.). Crystallization requires that the solution containing the substance to crystallize is supersaturated with respect to the latter, namely, that the solute concentration is higher than its solubility limit but lower than the precipitation threshold: an appropriately formulated crystallizing solution reduces the solubility of the substance (both in the case of small inorganic/organic molecules and biological macromolecules, such as proteins), enabling a



Crystallizing Solution, Fig. 1 Vapor phase transfer in membrane crystallizers. (a) On the crystallizing solution side, the solute concentration increases due to the solvent removal triggered by the gradient of vapor pressure between the two sides of the membrane. (b) In the case of

antisolvent membrane crystallizers, the solubility of the solute decreases due to the increase of the antisolvent concentration inside the crystallizing solution usually generated by a temperature difference between the two sides of the membranes

more easily reaching of the crystallization range, where spontaneous formation of the first crystalline nuclei and their next growth can occur. Usually, crystallizing solution consists of a precipitating agent, a substance whose concentration is inversely correlated to the solubility of the molecule to crystallize, and a buffer salt able to stabilize the pH during the crystallization process. In order to optimize the crystallization, additives, whose concentration is lower than that of the main components, can be added. In the case of crystallization of proteins, ligands and cofactors can be exploited to stabilize the protein or to increase its conformational purity. Notwithstanding it is common to classify the components of a crystallizing solution according to these three categories, a sharp distinction is not possible because a substance might act as precipitating agent in a given cocktail and be used as an additive in a different case. Besides to affect the solubility, the components forming the crystallizing solution have to weakly interact with the molecule of the substance to crystallize (Wilson 2003). Differently, stronger interactions make more soluble the substance to crystallize, while the absence of interactions drastically reduces the solubility, resulting in an amorphous precipitation. As the space of the conditions (nature and concentration of each component)

promoting weak interactions is usually very small, it is necessary to explore several formulations before obtaining the best one. One of the most used methods to deal with the crystallizing solution formulation problem is the multivariate analysis that allows testing several successful events of crystallization against a high-dimensional space represented by the crystallization conditions (Segelke 2001). Depending on the crystallization method, the concentration of each component of the crystallizing solution can vary or keep unchanged during the crystallization process: no change occurs in the case of the batch method where the level of supersaturation is directly adjusted on the crystallizing solution. Conversely, the component concentrations change when the supersaturation level is reached in the time by using vapor or liquid diffusion techniques. Techniques that exploit membranes to put in contact a crystallizing solution containing the molecule to crystallize and a stripping hypertonic solution or an antisolvent on the other side of the membrane (distillate side) belong to the latter category. Due to its hydrophobicity, membrane is not wet by the two liquids on the two sides and the flux of solvent molecules through the membrane can occur by vapor diffusion (Fig. 1a). Accordingly, it is possible to achieve a

fine regulation to the rate to which solute increases its concentration in the crystallizing solution by managing the transmembrane flux. Similarly, in the case of antisolvent membrane devices, vapor diffusion triggers the increase of the antisolvent concentration inside the crystallizing solution (Fig. 1b), resulting in a decrease of the solute solubility (Di Profio et al. 2009). By using hydrophilic membranes, it is possible to exploit liquid-phase transfer: in this case, crystallizing solution is directly pressed through a porous membrane in an antisolvent (or vice versa). This technique has been used to produce crystal of L-asparagine with narrow size distribution (Zarkadas and Sirkar 2006).

Cross-References

- [Crystallization](#)
- [Hydrophobicity](#)
- [Multivariate Analyses](#)
- [Solubility](#)

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Cutoff Membrane

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The membrane filtration is a very efficient and economical way for separating components that

are suspended in a liquid or mixed in the gas. The membrane is a physical barrier that allows certain compounds to pass through, depending on their physical and/or chemical properties. Therefore, the cutoff property of membrane is a significant parameter.

In the liquid separation process, a membrane filter comprises a membrane with a pore size between 5 nm and 50 μm . On the basis of the cutoff membrane rate, the membrane technologies can be classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) (Table 1). The MF membrane has pore sizes in the range of 0.1–5 μm and is capable of removing suspended particles like blood cell, microorganism, and latex emulsions. The UF membranes with pore sizes in the range of 2–100 nm can remove large molecules like albumin, bacteria, or pepsin. The cutoff membrane rate of UF can also be characterized in terms of the so-called molecular weight cutoff (MWCO), which is generally expressed in standard dalton (Da) or kilodalton (kDa) units. While this classification method is inherently deficient since the atomic mass does nothing to describe the actual size or geometry of a molecule, it remains the standard convention for UF membrane classification. NF membrane has a pore size less than 1 nm. It can separate small molecules like divalent salts, dissociated acids, and sugar. NF membranes are generally characterized by their ability to retain a divalent ionic species such as magnesium sulfate (MgSO_4) or calcium chloride (CaCl_2). The typical rejection rate of MgSO_4 might range from around 80 % to 98 %. RO membrane with pore sizes in the range of few angstroms can separate water molecules or ions like sodium and chloride on the molecular or ion level. The typical rejection rate of RO for NaCl can be on the range of 98–99.5 %, which is influenced by given pressure, temperature, and concentration conditions. However, the gas separation requires membrane with small pore size.

Many characterization methods like permoporometry, thermoporometry, mercury porometry, gas adsorption–desorption, nuclear magnetic resonance (NMR), and liquid–liquid porometry, along with several microscopic

Cutoff Membrane, Table 1 Cutoffs of different liquid filtration techniques

Micrometer	0.001	0.01	0.1	1	10	100	1000
Angstroms	1	10	100	1000	10 ⁴	10 ⁵	10 ⁶
Molecular weight	0.5	50	7000				
Substances to be separated	Solved salts		Viruses	Bacteria	Yeast		Sand
	Sugar	Albumin		Red blood cells			
Process	Reverse osmosis		Ultra filtration			Particle filtration	
		Nano filtration		Microfiltration			

techniques, have been used to characterize the membrane pore and pore size distribution. Each of these methods has different characteristics and relies on different theoretical considerations to be taken into account to convert the direct results into pore sizes. Among these techniques, the bubble point test has gained enormous relevance for the characterization of MF membranes. However, it cannot be properly applied to UF membranes due to the high pressure (more than 10 bar) necessary to evaluate pore with sizes below 0.1 μm . On the contrary, the liquid–liquid displacement porometry (LLDP) is very suitable for characterizing UF membranes at relatively low applied pressures. However, for the dense nonporous membrane such as NF, RO, and gas separation membranes, some experimental techniques such as positron annihilation lifetime spectroscopy, inverse gas chromatography, and Xe NMR are available for determining the average radius (1–10 Å) and the size distribution of the free-volume elements. And atomistic modeling can only explain the topology and structure of free-volume elements in polymers.

Generally, the selection of a membrane cutoff rating is 0.2–0.3 times the value of the molecular weight targeted for retention. Thus, prior to use, it is necessary to characterize physical

characteristics such as pore size distribution (and mean pore size), porosity (void volume), and tortuosity (or the relative length of the path of diffusion across the membrane material).

Cyclodextrin in Membranes

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Cyclodextrins have the unsurpassed ability to form inclusion compounds with suitable guest molecules. Interaction of native and modified cyclodextrins with cellular membrane was intensively studied in view of their large use as drug delivery systems. Moreover, cyclodextrins have found many potential applications in membrane science. In this latter case, in addition to the ability to form inclusion complexes, also the intrinsic chirality of the cyclodextrins and their enzyme-like behavior were exploited in membrane applications. Almost all the membrane processes are involved independently from their driving forces applied (Kozłowski and Sliwa 2008). Native

cyclodextrins, but also dimers, modified cyclodextrins, polymers, and specially cross-linked cyclodextrins were used. Cyclodextrin can be grafted to polymer chains, dispersed in casting solutions to form composite membranes, used as carriers in liquid membranes, bonded to ceramic membranes, or cross-linked alone or with suitable organic polymers. In this latter case, formaldehyde, glutaraldehyde, citric acid, hexamethylene diisocyanate, tetramethyl orthosilicate, as well as ethylene glycol diglycidyl ether were used as cross-linking agents. The main organic polymers used were PVDF, polyvinyl alcohol, polydimethylsiloxane, silicone rubber, polypyrrole, polyurethane, poly(*N*-isopropylacrylamide), polyamide-imide, polysulfone, PVC, polyacrylonitrile, PEEK-WC, as well as chitosan, cellulose, and cellulose diacetate. Flat sheet and hollow fiber membrane configurations were reported. Phase inversion technique and casting followed by a cross-linking reaction were the most used procedures to get cyclodextrin-containing membrane; however, other techniques were also employed, i.e., electrospinning. As carriers in liquid membranes, cyclodextrins allow the selective transportation of saccharides and to achieve good results in this difficult separation. Organic structural and geometrical isomer enrichments were obtained by using water-based liquid membranes. Liquid-liquid extraction was also used to separate racemic mixtures because the cyclodextrin nanocavity allowed the formation of diastereomeric complexes. Enantiomeric discrimination of native aromatic amino acids was also performed. Chiral enrichment of racemic chlorthalidone and propranolol was achieved using bulk liquid membrane containing cyclodextrin as a mobile enantioselective carrier. Because of their different ability to complex isomers, immobilized cyclodextrins also largely influenced permeation in dialysis membranes. In this way, *ortho*, *para*, and *meta* isomers of aromatic compounds were successfully achieved as well as the enantiomeric separation of aromatic amino acids. Pervaporation processes were also greatly influenced by the addition of cyclodextrins or cyclodextrin derivatives prevalently in PVA membranes. Thus,

propanol isomers, xylene isomers, and water/ethanol and water/1-propanol or 2-propanol were studied at length as were permeabilities greatly influenced by cyclodextrin contents. Pervaporation membranes were also produced by using polyurethanes polymers hosting cyclodextrins. This system was used essentially to separate phenol/water mixtures. Polyimide-based cyclodextrin-containing membranes found application in isopropanol dehydration and butanol isomer separation. Cyclodextrin was used in membrane reactors as an additive to obtain enantiomeric separation, being the reaction catalyzed by enzyme or exploiting the enzyme-like behavior of water-insoluble modified cyclodextrin dispersed in PEEK-WC membranes.

Polyimide polymer membranes added to cyclodextrins alone or grafted onto carbon nanotube surfaces have a relevant influence on CO₂/CH₄ as well as propane/propylene gas separation. The characteristics of cyclodextrins fit well with the requirements for membrane sensor-making. Depending on the cyclodextrins and membranes used, excellent selectivity toward glucose, tetracycline, several heavy metal cations, and even an enantioselective determination of R-clenbuterol was reported. In this latter case, a detection limit of 2.99×10^{-7} mol/L was reached. The introduction of cyclodextrins into the polysulfone membrane structure greatly influenced the rejection of humic acid and natural organic matter from water. Again polysulfone/CD membrane found uses in endocrine disruptors removal from water. Alternatively, acid dyes can be removed from wastewater by using a chitosan membrane modified with cyclodextrin. Ceramic membranes impregnated with cyclodextrin polymers are effective in facilitating polycyclic aromatic hydrocarbons' removal. In addition, the polyacrylonitrile membrane with triacetyl- β -cyclodextrin is able to reduce the amount of pesticides in citrus essential oil. Both hydrophobic β -cyclodextrin polymers in triacetate membrane and polypyrrole polymer membrane doped with sulfated α -cyclodextrin facilitate the transport of heavy metal cations from aqueous solutions. The high versatility of membrane processes allows the preparation of

composite Nafion membranes with sulfated- β -cyclodextrin. This induces a remarkable increase on proton conductivity with a very slight increase in methanol permeability. Even better results were achieved by using sulfonated PEEK membranes. Anion exchange membrane performances in electrodialysis processes are influenced by the introduction of cyclodextrins in the polymer network. Due to the changes in the hydrophilicity of the environment, transport of less hydrated anions decreased, while transport of strongly hydrated anions increased by enhancing the content of cyclodextrin. Minor application of cyclodextrins was also found in UF, NF, RO, temperature-controlled membrane processes, and a new drug delivery system.

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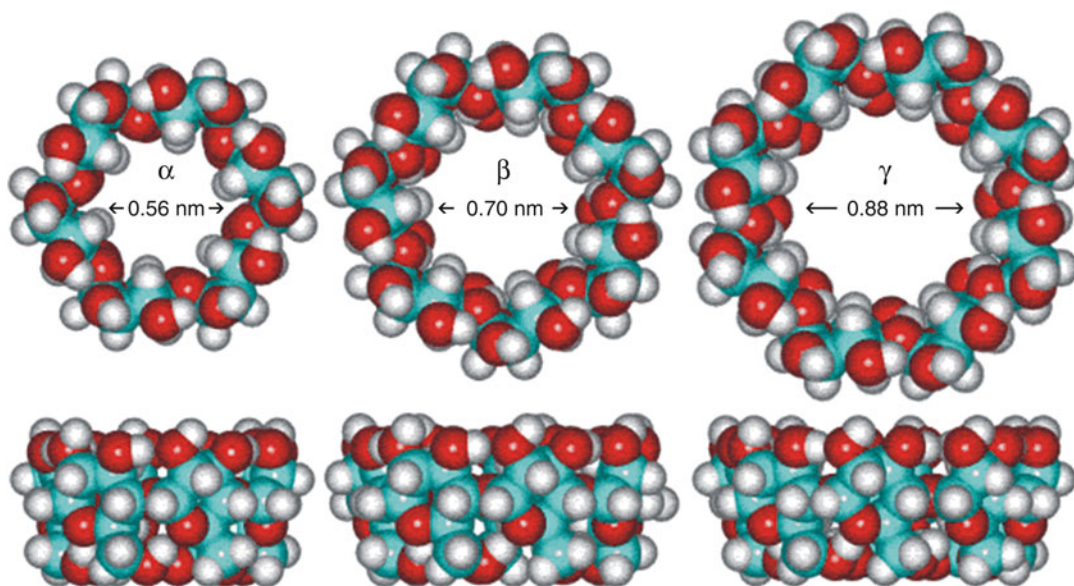
Cyclodextrins

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Cyclodextrins (Astray et al. 2009; Loftsson and Duchene 2007; Martin Del Valle 2004; Szejtli 1998; Szente and Szeman 2013) (Schardinger dextrins, cycloamylose, cyclomaltose) (Fig. 1) are cyclic nonreducing oligosaccharides obtained through the enzymatic degradation (*cyclomaltodextrin glucanotransferase*) of starch. They are made up of six, seven, or eight glucose units linked by 1–4 α glucoside bonds and have a typical truncated cone-like shape. They are named α -, β -, and γ -cyclodextrin, respectively. Larger cyclodextrins, i.e., δ and ϵ , are also known, but they are much more expensive, have a twisted structure, are less stable, and are of limited interest. The position of the atoms form a

lipophilic cavity surrounded by a hydrophilic rim being the OH groups located on the exterior edge. Primary hydroxyl groups are all located on the narrow edge of the truncated cone being the secondary positioned on the larger edge. The reactivity of the hydroxyl groups differs enough to be used in selective modification of the native cyclodextrins. Cyclodextrins were first discovered by French chemist A. Villiers in 1891 as a by-product in the production of dextrins. A few years later, Austrian chemist F. Schardinger isolated the strain on bacteria (*Bacillus macerans*) responsible for the synthesis of cyclodextrins. However, it was only through the work of Freudenberg in 1935 that the cyclic nature of cyclodextrin was discovered. The toroidal structure of cyclodextrins allows them to form inclusion compounds with a great set of molecules with suitable polarity and size. The polarity of the inner nanocavity is believed to be similar to an aqueous ethanolic solution. The inner cavities have a diameter in the range of 0.47–0.53, 0.60–0.65, and 0.75–0.88 nm, respectively. On the other hand, the height (0.79 nm) is the same for all three native types. Generally speaking, the internal diameter of the cavity mostly accounts for the encapsulation of the guest molecule. The smaller α -cyclodextrin complex compounds with linear aliphatic chains, β -cyclodextrin includes well aromatic structures, and γ -cyclodextrin accommodates larger molecules. All native cyclodextrins are quite safe and can be orally administered without toxic effects because they are not absorbed by the gastrointestinal tract. On the other hand, both parent α - and β -cyclodextrins are not suitable for parenteral administration. α - and γ -cyclodextrins have good water solubility, but β -cyclodextrins have limited solubility in water, i.e., 1.85 wt.% at room temperature. In any case, the water solubility of the parent cyclodextrins is much lower than corresponding linear oligosaccharides. Solubility increases to a large extent by increasing the temperature and/or pH. Inclusion compounds can be produced following several techniques such as grinding, freeze-drying, spray-drying, kneading, coprecipitation, melting, evaporation, etc. Hydrophobic molecules are incorporated into the cavity of cyclodextrins by displacing



Cyclodextrins, Fig. 1 Molecular structure of native cyclodextrins

water. This effectively encapsulates the molecule of interest within the cyclodextrin, rendering the molecule water soluble. When the water-soluble complex is diluted in a much larger volume of aqueous solvent, the process is reversed, thereby releasing the molecule of interest into the solution. The encapsulation of the guest molecules inside the cyclodextrin cavity leads to many changes in their physical-chemical properties. In particular, cyclodextrins can:

1. Increase the solubility of poor water-soluble molecules and drugs
2. Transform liquid in solid powder
3. Host volatile molecules in solid form
4. Mask smell and taste
5. Protect substances by light and oxidation
6. Act as enzyme-like catalysts
7. Act as inverse phase catalysts
8. Change membrane permeabilities

The abovementioned properties allow cyclodextrin to find many applications in cosmetics, separation, laundry, catalysis, drug delivery, analytical chemistry, food additive, agriculture, and chemical industries. Although several hundred cyclodextrin derivatives were already

reported in the literature, only few have found industrial application due to their superior performances and safe profile: hydroxypropyl β -cyclodextrin and sulfobutyl ether β -cyclodextrin. Random methylated β -cyclodextrin is also of interest but it cannot be used in drug delivery due to its toxic effects. In order to increase the stability constant of the inclusion complexes, dimer and trimer of cyclodextrin were synthesized as well as linear and cross-linked polymers. The latter can act as nanosponges, nanocontainers, or nanocarriers.

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Dead-End Filtration

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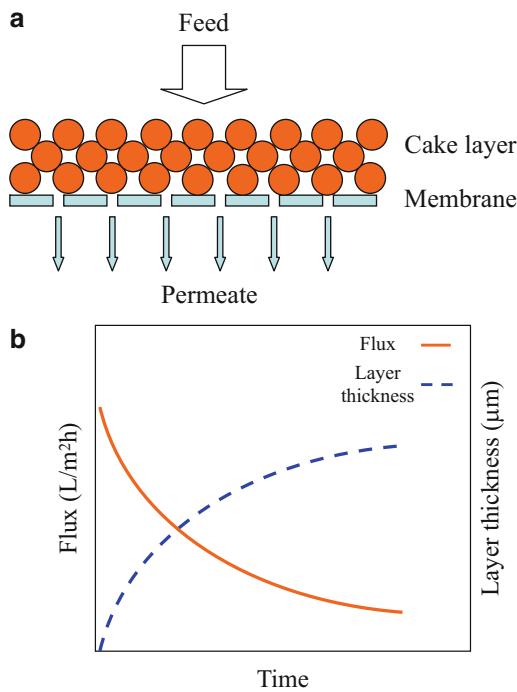
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The dead-end filtration is the one where the flow of water is perpendicular to the membrane surface (Fig. 1a). And the water is pushed through the membrane by pressure. All the water that is introduced in the dead-end cell passes through the membrane. In other words, there is no retentate. In dead-end filtration the retained particles build up with time on the membrane surface or within the membrane. In either case, the building particle would result in the increase of layer thickness and cause the permeate flux to decline (Fig. 1b). Thus, the dead-end filtration requires the stopping of filtration to clean or replace the membrane. Therefore, this type of filtration is also called batch filtration.

There are two types of filtration which can be employed in a dead-end filtration unit: constant flux and constant pressure. The dead-end filtration

with constant flux ensures that the permeate flux through the membrane remains constant. This filtration can be achieved by positive displacement pump. As the cake buildup increases with time, the pressure drop would increase so as to maintain constant flux. The constant flux strategy is usually applied in the industrial applications. Since the produced volume is a main operating goal. In another dead-end filtration mode of constant pressure, the permeate flux decreases as the cake build-up with the time. The constant pressure strategy is commonly chosen in the laboratory scale installations, because this is easy to implement on a small scale.

However, the dead-end filtration performance is often limited by fouling phenomenon owing to its filtration characteristics. Some strategies are employed to control membrane fouling, such as module design, pretreatment, or hydrophilic modification of membrane materials. Four distinct models based on Darcy equation can be used to describe the dead-end fouling behavior (Table 1). The relationships described were the complete blocking model, which assumes that each particle that deposits on the membrane will seal a membrane pore; the intermediate blocking model, which assumes that only a portion of the deposited particles will seal a membrane pore; the standard



Dead-End Filtration, Fig. 1 Schematic diagram of dead-end filtration (a) and representation of flux rates and layer thickness (b)

blocking model, which assumes that the pore volume will decrease proportionally to the filtrate volume by deposition of solids on the pore walls; and the cake filtration model, which assumes that the cake resistance is proportional to the filtrate volume by deposition of solids on the membrane surface.

The mathematical expressions for these laws are summarized in Table 1. For a constant pressure filtration mode, they have been reformulated in a common frame of power-law relationships (Hermia 1982):

$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV} \right)^n \quad (1)$$

Table 1 also presents the physical basis for each fouling mechanism and the corresponding n -value. Each of these mechanisms could be alone or in combinations, to explain experimental observations. Overall, the membrane fouling control is a key problem for the large-scale application.

Dead-End Filtration, Table 1 Fouling mechanisms and their corresponding physical basis (Grenier et al. 2008)

Fouling mechanism	n	Corresponding linear form	Physical concept	
Cake filtration	0	$\frac{dt}{dV} = \frac{1}{Q} = f(V)$	Surface deposit	
Intermediate blocking	1	$\frac{dt}{dV} = \frac{1}{Q} = f(t)$	Pore blocking and surface deposit	
Standard blocking	1.5	$\left(\frac{dV}{dt} \right)^{1/2} = Q^{1/2} = f(V)$	Pore constriction	
Complete blocking	2	$\frac{dV}{dt} = Q = f(V)$	Pore blocking	

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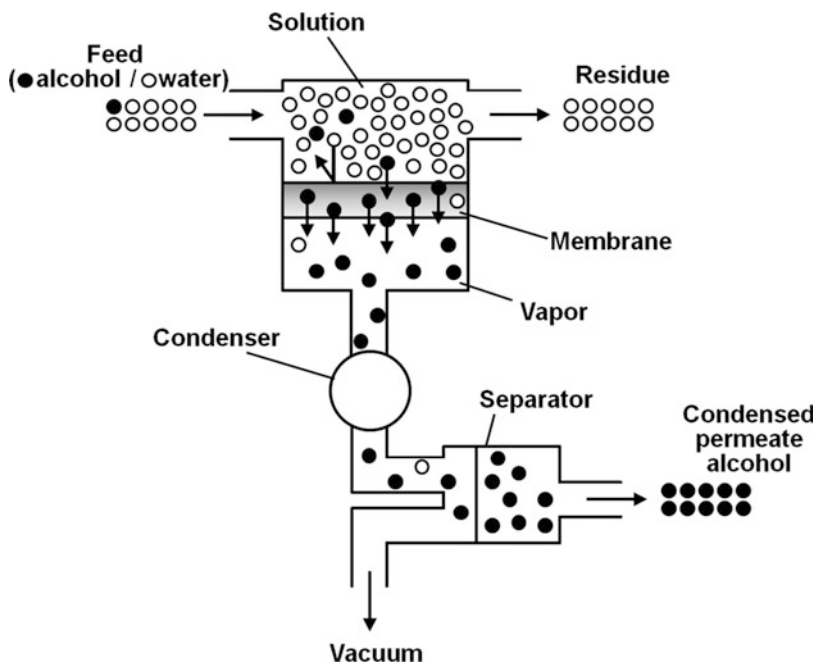
Dealcoholization by Pervaporation

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Dealcoholization by pervaporation (PV) is one of the most innovative processes for the selective separation and condensation of ethanol from a dilute aqueous solution of ethanol obtained from biomass fermentation (about 10 wt%) using PV method. The energy for bioethanol that is produced using distillation requires approximately 1.5 times than that obtained from ethanol fuel. Among them, about 70 % is estimated to be

consumed in distillation. Thus, dealcoholization by PV is efficient because of energy conservation and separation of an azeotropic mixture, which cannot be separated by distillation. In PV, a liquid mixture is supplied to a membrane on one side. The permeated components are evaporated from the other side (Fig. 1). Thus, the driving force of this process is a gradient of partial pressure or chemical potential located across a membrane. To enhance the flux or the total amount of the product, the permeated side is always maintained at a pressure below the saturated pressure of a given component, either under a vacuum or by sweeping the vapor using a carrier gas. The vapor at the permeated side is then condensed and recovered as liquid (Nagai 2010). The features of this method are: (1) increased separation performance from solution, diffusion, and vaporization; (2) the driving force of permeation does not depend on the pressure and is applicable to the organic liquid solution with high osmotic pressure; (3) PV does not need pressurization; (4) this method can be applied to separate the mixture solution, which cannot be done by distillation, for example, the separation of the thermal denaturation/thermally decomposable mixture, azeotropic mixture, near-

Dealcoholization by Pervaporation,
Fig. 1 Dealcoholization by a pervaporation process



boiling point mixture, and structural/optical isomers can be concentrated; (5) the reaction can be promoted because of the movement of the equilibrium reaction; and (6) the method does not pressurize, and no consolidation of the membrane occurs. The term PV is a compound word of Permeation and Evaporation. Moreover, it has been originated from the article of Kober (1917). There are two kinds of method for alcohol concentration by PV. The alcohol-selective method removes alcohol from the dilute alcohol aqueous solution of concentrated alcohol, whereas the water-selective method removes water at a high-concentrated alcohol solution. The materials differ according to their use. The alcohol-selective method uses silicone gum and poly(1-trimethylsilyl-1-propyne). By contrast, the water-selective method uses cellulose acetate and poly(phenylene oxide), which yield good results. Generally, the alcohol-selective method is called dealcoholization by PV. Researches on alcohol-selective permeable membranes are fewer than those on water-selective permeable membranes. In addition, membranes with performance that can be set in bench-scale plants have not been developed. Thus, the developments of alcohol-selective permeable membranes are delayed compared with that of water-selective membranes. The cause is due to the larger molecular size of alcohol molecules, which are permeated preferentially, compared with that of water molecules. When alcohol from alcohol aqueous solution is permeated preferentially, separation on the diffusion process cannot be expected in PV method based on a solution-diffusion mechanism. Thus, separation can be performed using the difference in the only solution process of both components of the membrane. However, the membrane is excessively swelled by very high affinity to alcohol because it is in direct contact with the mixture solution to be separated in PV method. Thus, permeability increases. However, the small molecular size of water enters the membrane by the plasticizing effect because of membrane swelling, which significantly reduces the selectivity to alcohol. To solve this problem, the balance of hydrophobicity and affinity of the membrane is examined by graft, copolymers, multiblock,

blend, and three dimensional structures by cross-link. In each case, there is a limit to improvement in separation performance by previous method because there is a discrepancy between affinity and swelling.

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Dearomatization by Membrane Operations

- [Aromatic and Nonaromatic Separation by Membrane Operations](#)

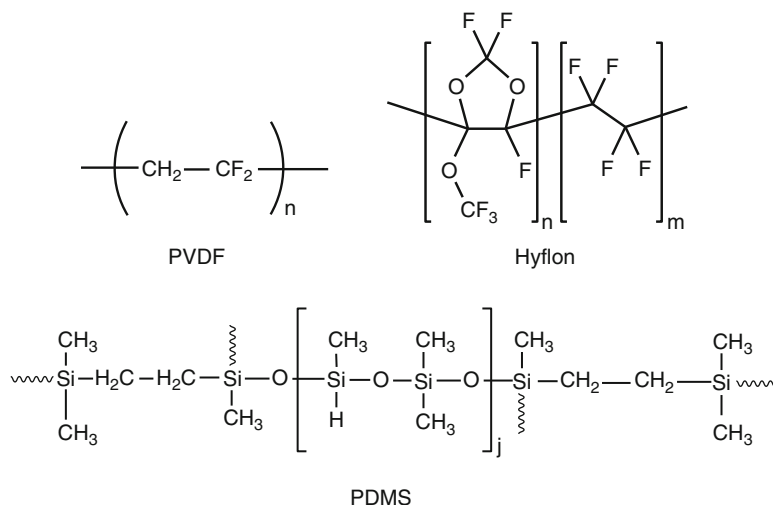
Decatungstate, Catalytic Membrane Containing

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Catalytic membrane containing decatungstate is a polymeric catalytic membrane applied on a lab scale in liquid phase photooxidation reactions (Drioli and Fontananova 2010).

The decatungstate ($W_{10}O_{32}^{4-}$) is a photocatalytic polyoxometalate (polyanionic metal oxide cluster of early transition metals) with remarkable properties for application in oxidation catalysis for fine chemistry and wastewater treatments.

In particular, decatungstate exhibits interesting properties for the photocatalytic detoxification of wastewater since its absorption spectrum ($\lambda_{\max} = 324 \text{ nm}$) partially overlaps the UV solar emission spectrum, opening the potential route for an

Decatungstate, Catalytic Membrane Containing,**Fig. 1** Chemical formula of the polymers used to prepare the catalytic membranes entrapping decatungstate

environmentally benign solar-photoassisted application (Texier et al. 1999).

However, decatungstate has also some relevant limitations: low quantum yield, small surface area, poor selectivity, and limited stability at pH higher than 2.5 (Mylonas et al. 1996).

Membrane technology can offer the possibility to overcome these limitations by the multi-turnover recycling associated to heterogeneous supports, the selectivity tuning as a function of the substrate affinity toward the membrane phase, and the effect of the polymeric microenvironment on catalyst stability and activity.

In this respect, the design of alternative heterogeneous photooxygenation systems able to employ visible light, oxygen, mild temperatures, and solvent with a low environmental impact (water or neat reaction) was investigated by the immobilization of the decatungstate in polymeric membranes (Bonchio et al. 2003; Carraro et al. 2006; Fontananova et al. 2006; Drioli et al. 2008).

The successful heterogenization was guaranteed by a proper choice of both the catalyst functionalization and the polymer material.

Considering the interest toward the photooxidation reactions of organic substrates, principally in aqueous phase, hydrophobic polymer materials were selected for membrane preparation: polyvinylidene fluoride (PVDF), Hyflon (a perfluoro amorphous polymer), and polydimethylsiloxane (PDMS) (Fig. 1).

These polymers don't absorb in the region of interest of the catalyst; moreover, they are characterized by a high chemical, thermal, and UV stability.

In order to improve the catalyst/polymer interactions and to avoid catalyst leaching out from the membrane, lipophilic and insoluble-in-water derivatives of the decatungstate were employed: the tetrabutylammonium salt $((n\text{-C}_4\text{H}_9\text{N})_4 \text{W}_{10}\text{O}_{32})$ and a fluorinated decatungstate $([\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_3]_3\text{CH}_3\text{N})_4\text{W}_{10}\text{O}_{32})$ (Bonchio et al. 2003; Carraro et al. 2006).

A membrane-induced structure-reactivity trend, which may be exploited to achieve selective processes, was observed in polymeric catalytic membranes prepared embedding decatungstate within membranes made of PVDF (PVDF-W10), PDMS (PDMS-W10), or Hyflon (Hyflon-W10).

The polymeric catalytic membranes were prepared by solvent evaporation (to obtain dense membrane) or nonsolvent-induced phase separation (to obtain porous membranes). The decatungstate was solubilized or dispersed in the casting solution and heterogenized in the polymer matrix during the membrane formation process.

One of the crucial aspects during catalyst heterogenization is the maintaining of its structural integrity. Solid-state characterization techniques, including Fourier transform infrared (FT-IR) analysis and UV-vis spectroscopy in

diffuse reflectance, confirmed that the catalyst structure and spectroscopic properties were preserved within the membranes.

The PVDF-W10 and PDMS-W10 photocatalytic systems were used for the selective photooxidation of water-soluble alcohols (Bonchio et al. 2003). A membrane-induced discrimination of the substrate results from the oxidations of a series of alcohols with different polarity, through comparison with the homogeneous reactions.

The PVDF-W10 membranes were also successfully employed in the aerobic photooxidation of phenol in water carried out in a membrane reactor operating with flow through the membrane (Drioli et al. 2008).

Polymeric catalytic membranes were also prepared by immobilizing sodium decatungstate ($\text{Na}_4\text{W}_{10}\text{O}_{32}$) (Lopez et al. 2006; Lopez et al. 2007) and phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) (Fontananova et al. 2006), on the surface of PVDF membranes modified by Ar/NH_3 plasma discharges.

The groups grafted on the surface were able to bind the catalysts dissolved in aqueous solution, forming charge-transfer complexes.

Surface diagnostic techniques such as X-ray photoelectron spectroscopy (XPS), contact angle measurements (CA), and RX maps were used to attest the surface modification.

The catalytic membranes showed superior performances (higher reaction rate) compared to the corresponding homogeneous catalysts, in the photooxidation of phenol.

The decatungstate in the form of tetrabutylammonium salt was also heterogenized in Hyflon membranes by dispersion in the polymeric solution obtained using Galden HT55 (a mixture of perfluoro-hydrocarbons) as solvent and successive solvent evaporation. However, the insolubility of catalyst in this solvent and the low affinity between the catalyst and the polymeric matrix induced the formation of irregular catalyst aggregates, not well dispersed in the polymeric matrix, which tend to

precipitate toward the down surface (Carraro et al. 2006).

On the contrary, in the case of the fluororous-tagged decatungstate, SEM images of the membrane surface and cross section highlighted a homogeneous distribution of the catalyst domains which appear as spherical particles with uniform size.

The dimensions of these clusters and, as a consequence, the surface area and catalytic activity of the decatungstate were modulated acting on the membrane preparation conditions and catalyst loading.

The catalytic Hyflon-based membranes were tested in batch solvent-free oxygenation of benzylic C–H bonds of the ethylbenzene at 25 °C under O_2 atm.

The key observation was provided by an increase of the selectivity toward the alcohol (product of interest) and a higher turnover number (TON) when the catalyst was heterogenized in Hyflon membrane in comparison with homogeneous catalysts or the catalyst heterogenized in PVDF.

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Decentralized Wastewater Treatment System

► Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study

Dechlorination Process

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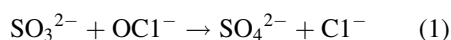
Dechlorination process is the process to remove the chlorine from chlorinated compounds or water that has been chlorinated.

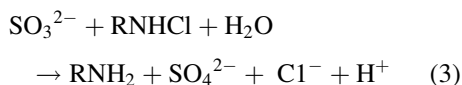
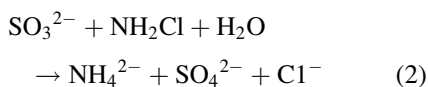
Dechlorination process has been widely used in water treatment, especially in the field of wastewater treatment and membrane process. Chlorinated compounds have been widely used as

refrigerant, agricultural fumigant, and solvent for metal degreasing and production of semiconductors in industrial processes for several decades (Kyunghoon and Woojin 2009). Chlorination has been used widely to disinfect wastewater prior to discharge. For these reasons, the chlorinated compounds and residual chlorine after disinfection are both contained in wastewater. However, the residual chlorine is toxic to many kinds of aquatic life, and the residual chlorine may also react with organic materials in the water forming chlorinated compounds, which have attracted an attention due to their carcinogenic and mutagenic characteristics. In membrane process, many kinds of membranes are also sensitive to residual chlorine, such as reverse osmosis (RO), nanofiltration (NF), and forward osmosis (FO). Consequently, dechlorination process is needed to remove the residual chlorine and degrade the chlorinated compounds.

The chlorinated compounds can be degraded by microbial and physical–chemical processes such as pump-and-treat, air sparging, and zero-valent iron passive barriers (Ma et al. 2003). The residual chlorine can be removed by absorption, chemical, and ultraviolet irradiation methods.

In membrane process, the feed must be dechlorinated to remove the residual chlorine and prevent the serious degradation of membrane chemical structure. Absorption and chemical methods are quite commonly used to dechlorinate in membrane process. The materials that have been proposed for dechlorination are granulated activated carbon (GAC), hydrogen peroxide (H_2O_2), ammonia (NH_3), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), and the sulfur(IV) species: sulfur dioxide (SO_2), sodium bisulfate (NaHSO_3), sodium sulfite (Na_2SO_3), and sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) (George and Lynn 1984). Some of the important reactions of sulfite with residual chlorine species are:





The residual chlorine in membrane process should be controlled in a certain range, which should rely on the dechlorination process. At present, few options exist for reliable close-to-zero levels of residual chlorine in the water, and the residual chlorine is needed to prevent the membrane from fouling as well (Kim et al. 2009). The rate of chlorine attack to the membrane depends on various feedwater characteristics, like pH and temperature, and different membranes also have not alike chlorine tolerance therefore, the different kinds of feedwater and membranes decide the residual chlorine concentration needed should be different. In addition, the excess of oxidizing agents, like chlorine, not only oxidizes microbiology but also oxidizes other organic molecules into organic pieces and is converted into assimilable organic carbon (AOC), which is good food for the bacteria (Redondo and Lomax 2001). Consequently, the residual chlorine should be monitored and adjusted in dechlorination process.

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Definition of Various Membrane Processes

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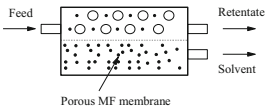
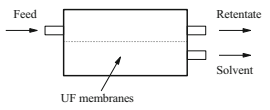
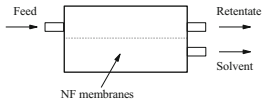
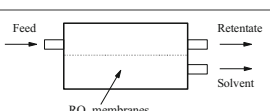
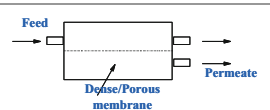
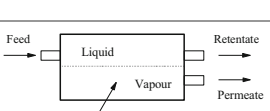
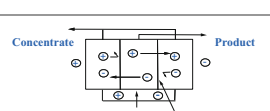
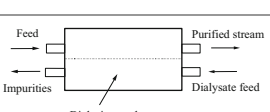
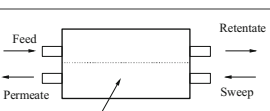
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Definition of Various Membrane Processes can be grouped according to the applied driving forces into: (1) hydrostatic pressure-driven processes such as reverse osmosis, nano-, ultra-, and microfiltration, membrane emulsification or gas separation, and pervaporation; (2) concentration gradient or chemical potential-driven processes such as dialysis, Donnan dialysis, pervaporation, and membrane contactors, such as membrane-based solvent extraction, membrane scrubbers and strippers, and osmotic distillation; (3) electrical potential-driven processes such as electrodialysis; and (4) temperature difference-driven membrane processes such as membrane distillation.

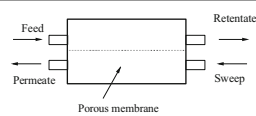
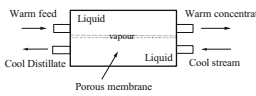
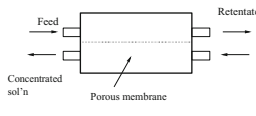
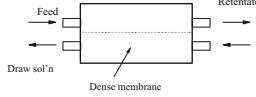
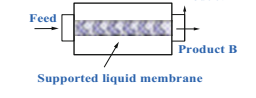
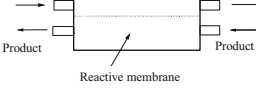
The molecular mixture which will be separated is referred to as feed, the mixture containing the components retained by the membrane is called the retentate, and the mixture composed of the components that have permeated the membrane is referred to as permeate (or filtrate in micro- and ultrafiltration). Table 1 lists the basic properties of membrane operations.

Definition of Various Membrane Processes, Table 1 Basic concepts of membrane operations

Process	Concept	Driving force	Mode of transport	Species passed	Species retained
Microfiltration (MF)		Pressure difference 100–500 kPa	Size exclusion, convection	Solvent (water) and dissolved solutes	Suspended solids, fine particulars, some colloids
Ultrafiltration (UF)		Pressure difference 100–800 kPa	Size exclusion, convection	Solvent (water) and Low-molecular-weight solutes (<1,000 Da)	Macrosolutes and colloids
Nanofiltration (NF)		Pressure difference 0.3–3 MPa	Size exclusion, solution diffusion, Donnan exclusion	Solvent (water), low-molecular-weight solutes, monovalent ions	Molecular-weight compounds >200 Da multivalent ions
Reverse osmosis (RO)		Pressure difference 1–10 MPa	Solution diffusion	Solvent (water)	Dissolved and suspended solids
Gas separation (GS)		Pressure difference 0.1–10 MPa	Molecular sieving, solution diffusion	Gas molecules having low-molecular-weight or high solubility diffusivity	Gas molecules having high-molecular-weight or low solubility diffusivity
Pervaporation (PV)		Chemical potential or concentration difference	Solution diffusion	High permeable solute or solvents	Less permeable solute or solvents
Electrodialysis (ED)		Electrical potential difference 1–2 V/cell pair	Donnan exclusion	Solutes (ions) small quantity of solvent	Nonionic and macromolecular species
Dialysis (D)		Concentration gradient	Diffusion	Solute (ions and low MW organics) small solvent quantity	Dissolved and suspended solids with MW >1,000 Da
Membrane contactors (MC)		Chemical potential, concentration difference, temperature gradient	Evaporation, diffusion	Compounds soluble in the extraction solvent; volatiles	Compounds non-soluble in the extraction solvent; nonvolatiles

(continued)

Definition of Various Membrane Processes, Table 1 (continued)

Process	Concept	Driving force	Mode of transport	Species passed	Species retained
Membrane-based solvent extraction (MBSX)		Chemical potential, concentration gradient	Diffusion partition	Compounds soluble in the extraction solvent	Compounds non-soluble in the extraction solvent
Membrane distillation (MD)		Vapor pressure gradient, temperature difference	Vapor transport	Water, solvent	Salts, nonvolatiles
Osmotic distillation (OD)		Vapor pressure gradient, hypertonic salt solution	Vapor transport	Water, solvent	Salts, nonvolatiles
Forward osmosis (FO)		Osmotic pressure	Diffusion	Water, solvent	Molecules, salts, ions
Supported liquid membranes (SLM)		Concentration gradient	Diffusion	Ions, low MW organics	Ions, less permeable organics
Membrane reactors (MR)		Various	Various	Permeable product/ controlled supply of reagent	Non-permeable reagents

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Dehumidification of Atmospheric Air by Membrane Technology

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Degenotoxification

► Genotoxin Removal

Degree of Mixedness

► Mixing Index

Synonyms

Membrane dehumidification of atmospheric air

Dehumidification of atmospheric air represents one large application opportunity for advanced membrane technologies. Air is used to supply oxygen for a number of industrial processes.

Dehumidification of Atmospheric Air by Membrane Technology, Table 1 Comparison of different air dehumidification technologies

Technology	Working principle	Feature
Membrane dehydration	Removal of moisture through a selective membrane with minimal changes to air temperature and pressure	A steady-state, continuous process
		A selective membrane is needed
		A driving force needs to be provided for moisture to transport across the membrane
Water condensation	Cooling of humid air below dew point for moisture to condense as liquid water or ice	Cooling of whole air stream is necessary
		Condensation adds latent cooling duty
Adsorption or solid desiccating	Capturing moisture on a solid adsorbent	Solid materials are durable and do not generate any environmental emission
		Heat of adsorption is released during capture
		Saturated adsorbent has to be regenerated by increasing temperature and/or reducing partial pressure of water vapor, and both sensible and latent heat need to be supplied for desorption
		Regenerated adsorbent needs to be cooled to capture temperature and heat of adsorption is released during capture
Absorption or liquid desiccating	Capturing moisture in liquid fluid	Fluid can be readily moved around
		Same heating and cooling cycles as adsorption are needed for regeneration of saturated fluid

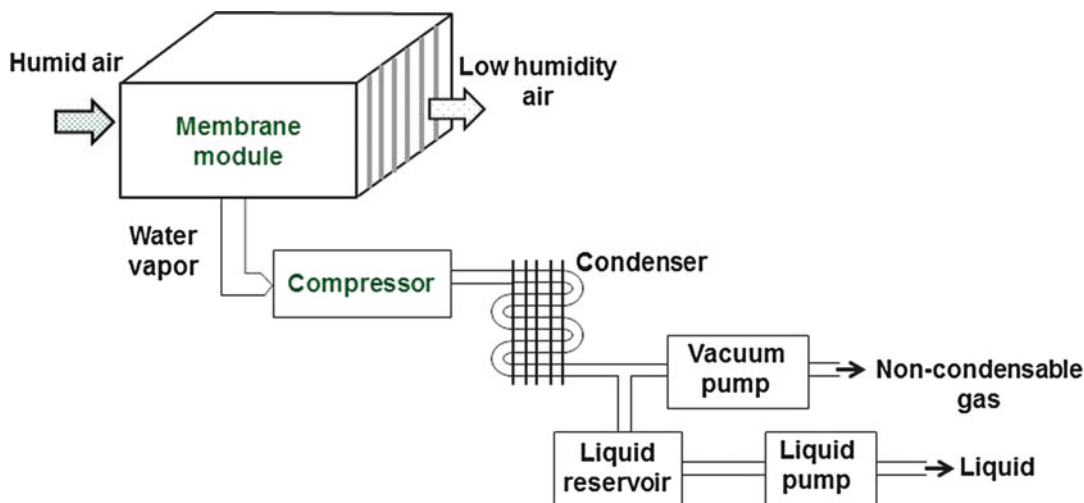
Moisture often needs to be removed when its presence presents a problem to downstream processes. For example, in oxygen production via cryogenic air separation, feed air needs to be adequately dehydrated to prevent formation of ice in the cooling equipment. Air dehumidification and conditioning in hot and humid climate are required to maintain comfort in buildings.

There are several commercial technologies for air dehydration, such as water condensation, solid adsorption, and liquid absorption. Their working processes and salient features are compared to membrane dehydration in Table 1.

As discussed above, the membrane dehydration is a steady-state process that works under feed air pressure and temperature. If humid air is cooled down or pressurized, moisture can be condensed out of the air as water. Cryogenic cooling of atmospheric air is often used in the industrial processes and in current building air conditioners for air dehydration. The main disadvantages of this method are the following: (i) the whole air stream has to be cooled down below water dew point and (ii) heat of condensation adds significant cooling duty. As a result, the energy efficiency is low. Solid adsorption and liquid absorption are widely used in the industrial gas and air drying

processes. A variety of solid adsorbents (e.g., silica gel, polymers, and zeolite) and liquid sorbents (e.g., LiCl, CaCl₂, and ethylene glycol) are available for capturing moisture at various temperatures and humidity levels. However, the desiccating material needs to be periodically regenerated by heating and cooling. The saturated desiccant is typically heated up to a much higher temperature than the capture to release the water as water vapor. Thermal energy has to be provided for the sensible heating and for compensating heat of desorption. After regeneration, the desiccant needs to be cooled down to the working temperature. During the capture process, heat of the adsorption (or absorption) is released to the dried air, which adds the sensible cooling duty of the air. Because of process complexity and significant thermal energy requirement, the adsorption or absorption method has found very limited applications in buildings.

Increasing energy demand in the building sector worldwide and growing concerns of indoor air quality have driven the development of new energy-efficient air dehumidification and conditioning technologies. Membrane dehumidification appears to be an attractive approach due to the following considerations. Different from



Dehumidification of Atmospheric Air by Membrane Technology, Fig. 1 Process scheme of dehumidification system

process industries, air in buildings does not need to get too dry, and high-degree dehumidification is not necessary. Membrane generally is effective for bulk separation. Membrane dehumidification does not generate any environmental pollution and is a green process. Lastly, membrane dehumidification has high thermodynamic energy efficiency.

One key challenge is the selective membrane. Due to handling of large gas flows and low partial pressures of water vapor in atmospheric air, the membrane has to be highly permeable to moisture. As expressed in the following equation, for a given dehydration rate (n_w) and partial pressure gradient of water vapor (Δp_w), the required membrane area decreases with increasing permeance in a reverse first order.

$$SA_m = \frac{n_w}{\text{Permeance} \cdot \Delta p_w}$$

Reducing usage of membrane area is not only beneficial to reduction of membrane cost but also enables a compact membrane module with minimal pressure drops for air to flow through.

The membrane also needs to have sufficiently high selectivity toward moisture over air. Air is non-condensable gas. As shown in the process flow of Fig. 1, any air leaked through the

membrane has to be pumped out of the water condenser into environment, while majority of the permeated water vapor is condensed. Thus, compression ratio for the leaked air is much greater than the permeated moisture, and air leakage would drastically increase power consumption of the vacuum pump. The previous study suggests that a H_2O /air separation factor above 200 be required for about 80 % dehumidification of 32 °C and 90 % RH air (Xing et al. 2013).

Other important factors about the membrane are durability and cost. The membrane has to be robust enough to be resistant to weathering, air contamination, and mechanical erosion in the duct. Also, the membrane surface has to be resistant to bacteria attachment and growth in warm and humid air environment. The membrane has to be cost-effective to penetrate the commercial building market.

Compared to extensive studies on membrane dehydration of water/alcohol mixtures, scientific publications on air dehumidification membrane development and tests are limited. Performance characteristics of a few membrane materials are compared in Table 2. The membrane permeance is given in both SI unit ($\text{mol}/\text{m}^2/\text{s}/\text{Pa}$) and gas permeation unit (GPU) for convenience of comparison. From an application point of view, the separation factor measured with actual humid air

Dehumidification of Atmospheric Air by Membrane Technology, Table 2 Air dehumidification performance characteristics of a few membrane materials reported in the literature

Membrane material	Testing conditions			Permeance		H ₂ O/N ₂ separation factor (selectivity)
	T (°C)	Permeate pressure (10 ³ Pa)	Feed gas	mol/(m ² Pa s)	GPU	
NaA/thin metal sheet (Xing et al. 2013)	32	0.31	Air+H ₂ O	6.8×10^{-6}	20,042	178
Polysulfone hollow fiber (Auvil et al. 1993)	32	4.7	N ₂ +H ₂ O	1.8×10^{-7}	529	50
Hollow fiber of stabilized liquid membrane (Bonne et al. 1990)	~27	0.54	Air+H ₂ O	N/A	N/A	N/A
Ionic liquid [emim] [Tf2N] (Scovazzo 2010)	31	0.69	Pure gas	2.1×10^{-7}	635	(3,843) ^a
Stabilized liquid triethylene glycol (Sijbesma et al. 2008)	15	N/A	Pure gas	5.7×10^{-8}	171–256	(1,700–2,500) ^a
	~30			-8.5×10^{-8}		
Stabilized liquid polyethylene glycol (M.W. = 400) (Sijbesma et al. 2008)	22	N/A	Pure gas	$\sim 5.0 \times 10^{-8}$	149	(~2,000) ^a
Sulfonated poly(ether ether ketone) (SPEEK) (Sijbesma et al. 2008)	30	<0.37	Pure gas	$\sim 5.0 \times 10^{-7}$	1,500	(300,000) ^a
PEBAX [®] 1074 (Sijbesma et al. 2008)	30	<0.37	Pure gas	$\sim 2.5 \times 10^{-7}$	750	(104,167) ^a
Zeolite 3A filled triethylene glycol (Ito et al. 1998)	22	0.44	Air+H ₂ O	3.8×10^{-9}	12	25
	~25					

^aThe selectivity was calculated as a ratio of relative permeability of single gas

is a meaningful parameter to quantify the membrane selectivity and calculate energy consumption. The separation factor was not reported in some of the literature. Instead, ratio of permeances measured with single gases was used to characterize the membrane selectivity. It should be alerted that such selectivity can differ drastically from the separation factor, because membrane structures and separation mechanisms under mixed gases could be substantially different from the single gas.

A NaA zeolite membrane supported on a thin porous metal sheet shows the highest H₂O permeance and excellent H₂O/air separation factor. These performance attributes of the NaA membrane can be explained by its microporous structure and molecular-sieving function. High selectivity is obtainable by eliminating or minimizing non-zeolite defects on the membrane. Since the selectivity results from selective H₂O adsorption at the entrance of zeolite pores, the membrane permeance can be proportionally

increased by reducing effective zeolite pore diffusion length without affecting the selectivity. The NaA framework is stable in air and various gas environments and is expected to possess excellent durability. It was reported that this kind of membrane enables development of compact membrane dehumidifiers with energy efficiency significantly higher than other dehumidification means at a competitive cost (Xing et al. 2013).

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Dehydration

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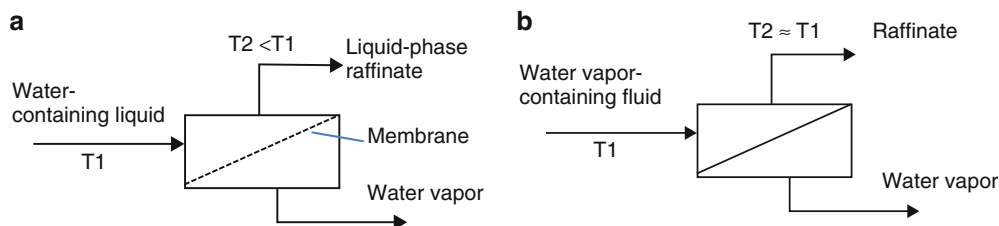
Dehydration is a common terminology but often has different meanings in different fields. In chemistry, dehydration is a chemical reaction process about conversion of one molecule into another one by removing H and O atoms as a water molecule, such as conversion of ethanol (C_2H_5OH) into ethylene (C_2H_4). In physiology and medicine, dehydration means the excessive loss of body water. Dehydration in food processing involves removal of water from various types of food for long-term preservation.

In the membrane field, dehydration generally refers to removal of water molecules from a water-containing fluid or mixture, i.e., it is a physical process. Two common membrane dehydration processes are illustrated in Fig. 1. In

pervaporation, water molecules are removed from water-containing liquid as water vapor and thus, a phase change of water occurs during the process. Due to significant heat of vaporization, the liquid feed temperature will be reduced without thermal energy inputs. Continuous supply of thermal energy is necessary to conduct pervaporation under a constant temperature. In the vapor-phase separation process, water vapor is separated out of a water vapor-containing fluid, and no phase changes are involved. Vapor-phase membrane separation is nearly an isothermal process.

The driving force for water molecules to move across the membrane is typically partial pressure gradient of water vapor. For a given feed fluid, partial pressure of water vapor in the permeate side can be lowered by pulling vacuum and/or introducing a sweep gas stream. Water transport across the membrane can also be driven by chemical potential gradient of water. For example, the forward osmosis process involves water transport from water-containing liquid of a lower solute concentration to liquid of a higher solute concentration, and a membrane gas/liquid contactor for gas drying involves transport of water from water vapor-containing gases into water-absorbing liquid. However, those membrane processes are viewed as different technologies from membrane dehydration.

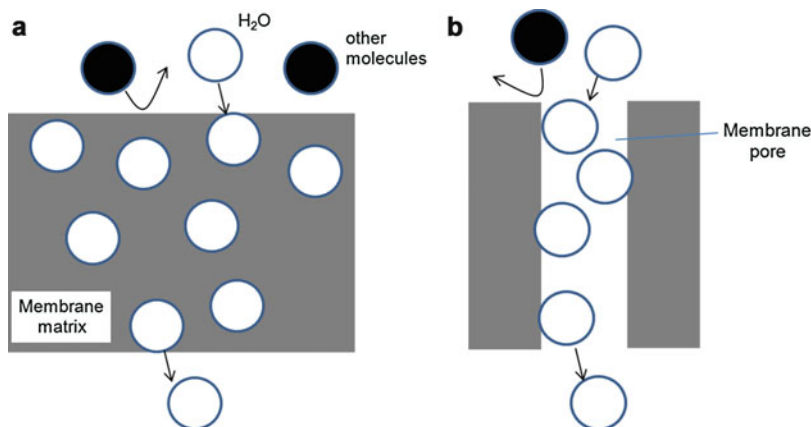
There are a variety of applications for membrane dehydration. Dehydration is necessary for production of pure or anhydrous alcohols, because a water-alcohol mixture is often produced by fermentation or catalytic reactions from feedstock of sugars, corn, cellulose, or syngas. Ethanol fuel production represents one major application of dehydration technologies, and its worldwide production capacity reaches about 85 billion



Dehydration, Fig. 1 Common membrane dehydration processes. (a) Pervaporation. (b) Vapor-phase separation

Dehydration,

Fig. 2 Separation mechanisms of dehydration membrane. (a) Solute diffusion in dense membrane. (b) Molecular sieving in microporous membrane



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liters/year in 2012. Successful development of cellulosic ethanol technologies is expected to lead more growth of ethanol fuels. Methanol is another commodity chemical with a large market. Water is miscible with a number of solvents and chemicals, such as acetic acid, acetone, and tetrahydrofuran. Dehydration of these solvents is involved in a range of industrial chemical conversion processes. The presence of water in industrial gases is ubiquitous. Air dehumidification and natural gas dehydration are examples of significant industrial gas drying processes.

One salient feature for the membrane dehydration process is molecular separation functions of the membrane. Removal of free water from slurry, i.e., separation of water from particulates, is typically referred as dewatering processes. The membrane allows permeation of water molecules while blocking other molecules. Because of the molecular separation function, the membrane dehydration provides significant advantages over conventional evaporation and gas drying technologies. The vapor-phase membrane separation is a steady-state process operating under constant temperature and pressure, as compared to periodic switches between adsorption (or absorption) and regeneration required for the solid (or liquid) desiccating process. For separation of a water-miscible liquid, the membrane dehydration is not limited by thermodynamic gas/liquid equilibrium such as co-boiling that often occurs in alcohol-water distillation processes. The membrane

dehydration is considered as an energy-efficient and compact process.

A number of membrane materials have been studied, and some of them are commercially developed for the dehydration application. They can be classified into two groups (Fig. 2): dense and microporous. The dense membrane provides selective absorption of water over other molecules. The separation mechanism can be described by the solute diffusion model. Most polymeric membrane materials fall into this category, which include polyvinyl alcohol (PVA), chitosan, alginate, polysulfone (PSF), polyimides, polyamides, polyaniline, and polyelectrolyte membranes such as cation-exchanged Nafion. Separation in a microporous membrane is mostly achieved through molecular sieving based on molecular sizes and/or selective adsorption of water at entrance of the membrane pore. Microporous zeolite, silica, and carbon are common membrane materials. Water molecule is often the smallest one in a mixture, and selective separation can be realized by making the membrane pore size small enough. However, the small pore size reduces molecule diffusion rates and may have a negative impact on flux. Molecular sieving based on selective water adsorption enables achievement of both high flux and selectivity (Zhang and Liu 2011). Some of zeolite frameworks, such as NaA, ZSM-5, and X-type and Y-type zeolite, have the pore size larger than that of water molecule but can be very selective toward water adsorption

over other molecules. Permeation of the other molecules is blocked due to adsorption of water molecules at the entrance of the zeolite pore, although the pore can be permeable to the other molecules in the absence of moisture.

The membrane dehydration performances are characterized by flux (J_w), permeance (P_w), and separation factor ($S_{w/i}$), which can be calculated from experimental measurements as follows:

$$J_w = \frac{\Delta n_w}{A_m \cdot \Delta t}$$

$$P_w = \frac{J_w}{p_{w,F} - p_{w,P}}$$

$$\alpha_{w/i} = \frac{(y_w/y_i)_P}{(x_w/x_i)_F}$$

where Δn_w is the amount of water collected in the permeate side of a membrane during a sampling period of time Δt , A_m is the membrane surface area exposed to the feed, $p_{w,F}$ is partial pressure of water in feed side, $p_{w,P}$ is partial pressure of water in permeate side, y_w and y_i are the respective molar fraction of water and specie i in the permeate side, and x_w and x_i are the respective molar fraction of water and specie i in the feed side.

The membrane materials and separation performances studied for the dehydration applications are well summarized in recent reviewing articles (Chapman et al. 2008; Wee et al. 2008; Bolto et al. 2012). The flux and separation factor reported for polymeric membranes are ranged from 0.01 to 1.0 kg/m²/h and from 10 to 1000, respectively, over a range of operation temperature from 25 °C to 80 °C. The microporous silica membrane has a higher flux and separation factor at comparable separation temperatures. The zeolite membrane shows the highest flux and separation factor. The flux and separation factor reported for separation of 10 wt.% water in ethanol with zeolite membranes (Zhang and Liu 2011) can be as high as 10 kg/m²/h and 10,000, respectively. The zeolite membrane can be used for both pervaporation at low temperatures and vapor-phase separation at high temperatures (above

100 °C). It should be noted that flux is a strong function of testing conditions. For a given membrane, water flux tends to increase with water content in the feed and with the separation temperature. Permeance should be a better parameter to characterize a membrane's throughput. However, this parameter was seldom reported in the literature. The permeance is estimated to vary over a wide range from 1.0E-5 to 1.0E-9 mol/m²/s/Pa among different membranes.

Selection of a suitable membrane for a given application depends on specific properties of the water-containing fluid. The material has to be chemically and physically stable under the separation conditions that the membrane structure can be maintained intact for a long time. For example, NaA is a commonly studied zeolite membrane for dehydration but it is not stable in acidic solutions. For dehydration of acetic acids, the more stable ZSM-5 and T-type zeolite materials are suggested. Pure zeolite membranes were considered difficult to prepare. To overcome the shortcomings with pure polymeric and ceramic membranes, researchers proposed mixed matrix membranes (MMM) comprising a polymeric base into which an inorganic material is dispersed and locked. The rationale is that some drawback associated with the polymeric material can be mitigated by incorporation of inorganic particles of durable structures, and MMM products may be produced with the manufacturing processes similar to polymeric membranes. There could be a variety of combinations from two groups of materials. Researchers have been actively exploring unique performance attributes of the mixed matrix membranes.

Membrane dehydration has found some industrial applications at relatively small scales so far. It is expected that widespread applications may become possible by lowering the membrane cost and enhancing productivity through continuing innovations.

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Dehydration of Solvents with Membranes

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Purification processes are required in the chemical industry in order to obtain a high purity of raw materials, intermediates, or end products. Separation of compounds from a mixture requires energy, and in many cases, the separation is difficult to perform due to the high energy consumption and high cost. The chemical or physical properties (e.g., molecular size, vapor pressure, freezing point, affinity, charge, density, and the chemical nature) of the target compounds are important factors in determining the viability of the separation process (Lee and Lai 1994; Mulder 1996). Solvent removal from dilute solutions via membrane filtration effectively leads to solute enrichment, but may just serve as a means to purify the solvent. Membrane processes are significantly advantageous in some applications (e.g., hemodialysis, azeotrope splitting, bioseparations, ultrapure water, fuel cells) while competing on equal terms with other traditional processes (Böddeker 2008). In membrane processes, the aim is to allow only one compound to pass through the membrane matrix while hindering penetration of other compounds. Reverse osmosis and pervaporation are the most common membrane processes for **dewatering of solvent**. In bioseparation, for instance, reverse osmosis membranes are capable of concentrating

bioorganic solutions under “mild” (low temperature) conditions by retaining aroma compounds. However, the principal and practical limitation which needs to be overcome is the osmotic pressure limitation. For example, the minimum pressure to dehydrate wine (11.9 % EtOH) by an ideally hydrophilic barrier is 64 bar; conversely, at least 860 bar is needed to remove pure ethanol from wine through an organophilic barrier. Removing water from the ethanol-water azeotrope (4 wt% H₂O at 78 °C) by reverse osmosis would require pressures in excess of 2000 bar; the other way around is meaningless (Böddeker 2008). As an alternative, pervaporation can be implemented. This process may involve a drastic reduction of the activity of the permeate by causing it to evaporate. Pervaporation can be potentially applied in the dewatering of organic liquid such as alcohols, ketones, and ethers among others. Although most of the installed solvent dehydration systems are applied for ethanol dehydration, dehydration of other solvents, including isopropanol, glycol, acetone, and methylene chloride, can be considered.

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Dehydrogenation Reactions

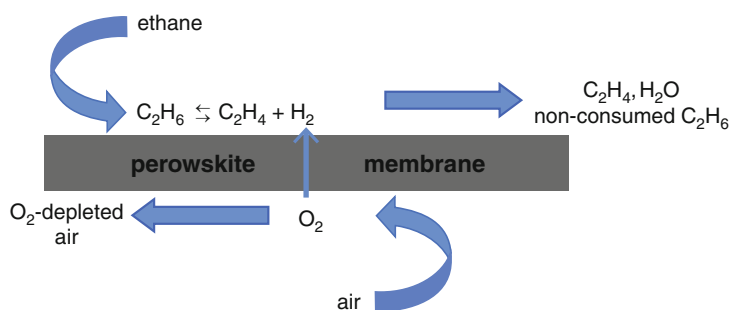
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Dehydrogenations of aliphatic or cyclic hydrocarbons are under technical condition thermodynamically controlled, i.e., the reaction takes place near

Dehydrogenation Reactions,

Fig. 1 Principle of a 2-step oxidative ethane dehydrogenation in an oxygen-transporting membrane reactor with a perovskite membrane



at the equilibrium alkane $\rightleftharpoons$ olefin + H_2 . There are hundreds of papers describing an increase of the alkane conversion and an increase of the olefin yield, if hydrogen is removed through a hydrogen-selective membrane from the reactors. Numerous hydrogen-selective membranes have been evaluated in dehydrogenation reactions, most often Pd-based membranes as compact foils or supported thin layer, pure Pd or as alloy with Ag or Cu, zeolite-based membranes, but also metal oxide membranes prepared via the sol-gel route or carbon membranes prepared by pyrolysis. For details, see (Dittmeyer and Caro 2008; Caro 2010). Interestingly, besides alkane conversion and olefin yield, also the olefin selectivity increased in comparison with classical fixed or fluidized bed reactors since the removal of hydrogen suppresses hydrogenolysis.

However, for all membrane-supported dehydrogenation reactions with hydrogen removal, it was found that after an initial improvement of alkane conversion and olefin yield, because of the hydrogen drain-off, a severe coking of the catalyst and the membrane is observed which causes the conversion and yield to be after 30 min–2 h below those of a packed bed reactor. The development of coke-resistant catalysts and membranes could not compensate this negative influence. Therefore, the scientific interest in dehydrogenation reaction dropped dramatically within the last decade.

However, there is a new concept to support dehydrogenation reactions by a selective in situ combustion of the hydrogen using oxygen-transporting membranes according to

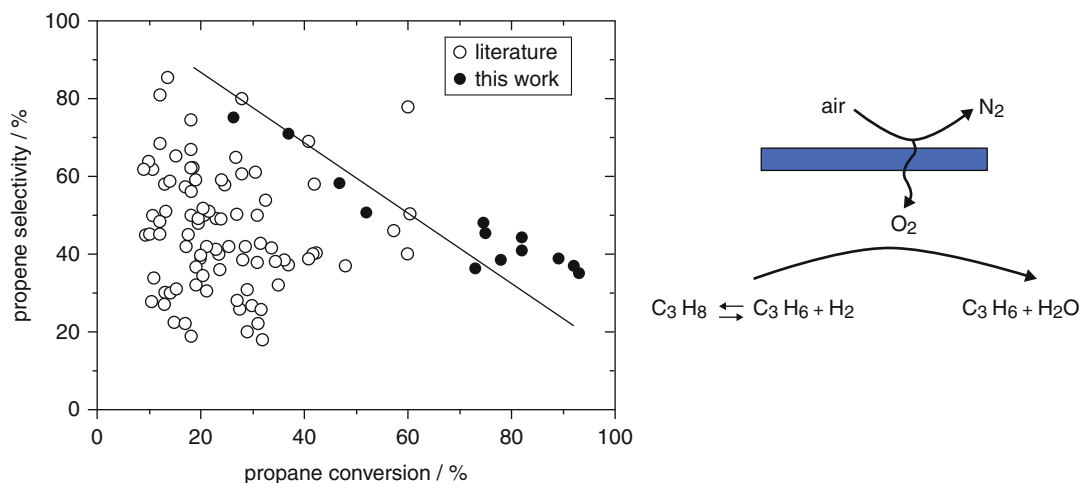
alkane + oxygen $\rightarrow$ olefin + water (steam) (Czuprat et al. 2009, 2010). The problem to be solved consists in the selective combustion of hydrogen in the presence of the alkane and olefin molecules. However, because of the higher reactivity of hydrogen in comparison with the hydrocarbons, this problem could be used, by using two catalysts: one catalyst for the dehydrogenation and the other one for the selective hydrogen combustion.

On the one-hand side, hydrogen is lost by combustion; on the other hand, in addition, in the boosting of alkane conversion and olefin yield, there are three advantages:

1. Hydrogen combustion brings heat for the endothermic dehydrogenation.
2. Steam suppresses coking of catalyst and membrane.
3. Steam dilutes the reactants which is favorable for thermodynamic reasons (shift of the equilibrium) (Fig. 1).

Principle of the oxidative ethane dehydrogenation in a membrane reactor with selective in situ combustion of hydrogen using an oxygen-transporting perovskite hollow fiber membrane (Czuprat et al. 2009) (Fig. 2).

Propene selectivity as a function of the propane conversion in the membrane reactor with oxygen-transporting hollow fiber perovskite membrane (filled spheres) in comparison with the best literature data for the oxidative dehydrogenation of propane (empty spheres) (Czuprat et al. 2010).



Dehydrogenation Reactions, Fig. 2 2-step oxidative propane dehydrogenation as described in Figure 1 for ethane

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Dehydroisomerization of N-Butane to Isobutene

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Isobutene is a valuable intermediate in the petrochemical industry, used as a raw material in several commercial processes to produce, for instance, organic acid (methacrolein and methacrylic acid), fuel additive (ethyl *tert*-butyl and methyl *tert*-butyl ether), and rubbery materials (polybutene, isoprene). Isobutene can be

obtained as a by-product from an oil refining process (e.g., cracking for ethylene production) or produced by converting normal butane by means of a two-stage process, isomerization and dehydrogenation (Romanow-Garcia et al. 2007; Obenaus et al. 2005; Buonomo et al. 1997). Butanes can be isomerized to isobutane and then dehydrogenated to the corresponding olefin; alternatively, normal butane may first be dehydrogenated to normal butene and then, subsequently, isomerized to isobutene. The catalysts, reaction conditions, and technologies needed for each of these stages are different, setting thus an economic penalty to the composite two-stage process.

Some alternative ways to produce isobutene are by dehydration of isobutanol (also by enzymatic dehydration) and by fermentative route. Although biological isobutene formation is known since the 1970s, extensive metabolic engineering is required to achieve economically viable yields and productivities (van Leeuwen et al. 2012).

An interesting alternative to the two-stage process is a one-step process, allowing direct conversion of *n*-butane to isobutene by means of a *dehydroisomerization reaction* (United States Patent 3; Li and Iglesia 2008).

n-Butane dehydroisomerization (reaction III) involves two equilibrium reactions: dehydrogenation

of n-butane (reaction I) and skeletal isomerization to isobutene (reaction II); both equilibria limit the possible yield of isobutene (Pirngruber et al. 2000).

n-butane $\leftrightarrow$ n-butene + H ₂ $\Delta H_{\text{Reaction}}$ (@25 °C) = 130 kJ mol ⁻¹	(Reaction I)
n-butene $\leftrightarrow$ isobutene $\Delta H_{\text{Reaction}}$ (@25 °C) = -17 kJ mol ⁻¹	(Reaction II)
n-butane $\leftrightarrow$ isobutene + H ₂ $\Delta H_{\text{Reaction}}$ (@25 °C) = 113.7 kJ mol ⁻¹	(Reaction III)

It is believed that dehydroisomerization proceeds through a transient intermediate stage wherein normal butenes are produced which are then subsequently isomerized (United States Patent 4). Due to the endothermicity of dehydrogenation (reaction I), dehydroisomerization has to be carried out at high temperatures (above 400 °C). The reaction is favored at low pressure occurring with a mole number increase. Formation of by-products occurs as a consequence of some typical reactions side. Butane protolytic cracking over acid sites and hydrogenolysis over metal lead to methane, ethane/ethane, and propane/propene formation. Most of the by-products originate from secondary reaction of the butenes formed, which are significantly more reactive than butane.

To carry out the dehydroisomerization of n-butane to isobutene, two options have been taken into account: the first one involves the use of a two-bed system with a dehydrogenation catalyst in combination with an isomerization catalyst (United States Patent 5; Byggningsbacka et al. 1998). The other approach uses a bifunctional catalyst system. In the open literature, bifunctional noble metal(s)-modified acidic supports have been reported (Pirngruber et al. 1999; Derouane-Abd Hamid et al. 2000). It is generally assumed that the dehydrogenation is the primary reaction step which occurs over the metal sites; then the n-butenes produced are successively isomerized to isobutene over the Brønsted acid sites. These kind of bifunctional catalysts have to be optimized with respect to their dehydrogenation and isomerization activity, as well as their stability toward deactivation. Concentration of acid sites, metal loading, and metal dispersion are some key factors. In particular, it has been

found that n-paraffins can be dehydroisomerized to iso-olefins in a single step, by using a catalyst composition in which the support has low acidity. Metal dispersion affects the selectivity toward reaction products; high dispersion in the pores of the support seems to lead to a very low dehydrogenation activity and consequently to a lower n-butene and isobutene formation. Chromium or platinum catalysts have generally been employed for dehydrogenation. A number of solid acids, which includes ferrierite, SAPO (silicoaluminophosphates), alumina, and zeolites, can be used as support. Several zeolite-supported platinum catalysts, such as Pt-ZSM5, Pt-ZSM11, and Pt-MCM22, have been explored (Derouane-Abd Hamid et al. 2000; Bee Derouane-Abd Hamid et al. 2000; Gulin Selda et al. 2008; Megumu et al. 2002). Bimetallic/multimetallic systems on acid support (Pt,Re/[B]-ZSM-11, PtSn on SAPO-11) have been also investigated due to the fact that they may exhibit better catalytic performances than corresponding monometallic samples (Gulin Selda et al. 2008; Megumu et al. 2002; Ponc and Bond 1995; Bond 1991).

Research activity on dehydroisomerization reaction is going on, and, in the future, it can become a feasible alternative reaction route to produce isobutene.

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Deionization by Membrane Operations

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Deionization, or desalination, is the process in which salt ions are removed from a polar liquid, which is virtually always water. Water deionization and water desalination are generally considered as synonyms, though deionization can be applied in a more restricted sense to denote those

processes where during water treatment cations move in the one direction and anions in the other direction.

Of course, during deionization, the total removal rate of anions (times their charge number) must equal the total removal rate of cations (time charge), to keep the produced effluent water electroneutral (conserve electroneutrality). The condition of electroneutrality will hold both for the produced freshwater and for the produced concentrate, the brine.

To make ions go in different directions, deionization processes in the limited sense as defined above make use of electrical field effects, i.e., by applying an external current to a water flow cell or system, ions in the water are induced to move in the electric field, with cations moving to positions of lower electrical potential (i.e., in the direction of the field strength), while anions move in the opposite direction.

The most well-known membrane process for deionization is electrodialysis and the various modifications thereof, including electrodeionization, a process in which ion-exchange resin particles fill the water flow channels in between the ion-exchange membranes and electrodialysis reversal, a modification of electrodialysis in which the applied electrical current is temporarily reversed during short periods of time to abate biofouling and scaling on the membranes (Sonin and Probst 1968; Strathmann 2010; Nikonenko et al. 2010; Andersen et al. 2012).

A novel deionization technology making use of membranes is membrane capacitive deionization in which ion-exchange membranes are placed in front of porous electrodes (either in the form of freestanding membranes or as a coating on the electrode) to capacitively remove salt from water in a cyclic process, i.e., ions are temporarily stored in the electrodes in one phase of the cycle and are released again during the phase where a brine is produced (Lee et al. 2006; Li and Zou 2011; Biesheuvel et al. 2011; Nie et al. 2011; Zhao et al. 2012).

Cross-References

► [Membrane Capacitive Deionization](#)

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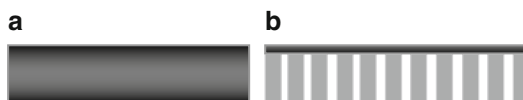
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Dense Membranes

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Dense membranes consist of dense structure presenting no detectable pore at the limits of electron microscopy. A mixture of molecules is transported through dense membranes by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. Dense membranes may have a symmetric or an asymmetric structure (Fig. 1). The first type has a uniform composition and structure over the entire cross section, and the thickness of the entire



Dense Membranes, Fig. 1 Schematic drawing illustrating the **a** symmetric and **b** asymmetric structures of dense membranes

membrane determines the flux. These types of membranes are also named homogeneous (dense) membranes. The asymmetric membrane consists of thin and dense selective layer (skin) supported on a much thicker microporous support layer that provides mechanical support.

The surface layer performs the separation, and it is the principal barrier to the flow through the membrane (Strathmann et al. 2006). They can be prepared from a large number of different materials: inorganic (metals, ceramics) or organic (polymers).

Inorganic materials generally possess superior chemical, mechanical, and thermal stability relative to polymeric materials. However, these materials have the disadvantages of being very brittle and more expensive than the organic materials. The dense inorganic membranes, extensively studied in the past decade, include metallic membranes, primarily palladium alloy membranes used for hydrogen separation. Generally, there are three techniques for coating metallic thin films onto porous metallic or ceramic supports: electroless plating, chemical vapor deposition (CVD), and physical sputtering. Electroless plating is a method of metal plating by autocatalytic chemical reduction of the corresponding metal ions with simultaneous oxidation of a reducing agent. This technique can be applied for forming metal coatings even on nonconductive supports such as porous ceramic or glass. In CVD, a volatile component of coating materials is thermally decomposed on the surface of the heated substrate to form a thin film or coating. In physical sputtering, a thin continuous film is deposited on the porous substrate by the bombardment with high-energy particles on the support (Adhikari and Fernando 2006).

The dense polymeric membranes are produced mainly by phase inversion process and coating

technique. The phase inversion is a process where a polymer is transformed in a controlled manner from liquid to a solid state. The process of solidification is very often initiated by the transition from one liquid state into two liquids (liquid-liquid demixing). At a certain stage during demixing, one of the liquid phases (the high polymer concentration phase) will solidify so that a solid matrix is formed. The phase inversion can be induced by solvent evaporation, precipitation from the vapor phase, and thermal and immersion precipitation. Making dense membrane by coating involves a two-step process. One is the preparation of a suitable porous support obtained by phase inversion, and the second is the preparation of the barrier layer on the surface of the support. Several techniques can be used to apply a thin top layer on support such as dip coating, spray coating, spin coating, grafting, plasma polymerization, interfacial polymerization, and in situ polymerization to achieve these membranes (Mulder 1996). Coating technique is used to prepare thin and dense structure, possessing high flux.

Dense membrane is used mainly to separate components which are similar in size but have different chemical nature in processes such as reverse osmosis, gas and vapor separation, and pervaporation. The transport of gas, vapor, or liquid through a dense membrane can be described in terms of a solution-diffusion model. According to this model, permeant molecules are dissolved into the entrance face of the membrane and diffuse across the membrane matrix, then dissolved species are desorbed in the downstream face of the membrane. The reverse osmosis process uses a large pressure difference across the membrane to separate water from salt solutions. In pervaporation, the pressure difference across the membrane is small, and the process is driven by the vapor pressure difference between the feed liquid and the low partial pressure of the permeate vapor. Gas permeation involves transport of gases under a pressure or concentration gradient (Baker 2004). The separation of the various components of mixture is directly related to their transport rates within the membrane phase, which is determined by their diffusivities and concentration in the membrane matrix. Therefore, the performance of membrane is determined by intrinsic properties

Dense Membranes, Table 1 Applications of processes based on dense membrane

Type of process	Applications	Polymeric membrane
Reverse osmosis	Desalination of brackish water and seawater	Cellulose acetate
	Concentration of solutions of food products, pharmaceutical solutions, and chemical streams	Aromatic polyamide Sulfonated polysulfone
	Wastewater treatment	Polybenzimidazole
Gas separation	Separation of nitrogen from air	Polymers of intrinsic microporosity (PIMs) polydimethylsiloxane
	Removal of water from air	
	Recovery of hydrogen from ammonia purge gases	Perfluoropolymer Teflon AF 2400
	CO ₂ separation from flue gas streams	Polyimides
Pervaporation	Removal of volatile organic compounds from wastewater or gas streams	Polyurethane Polydimethylsiloxane
	Recovery of aroma and biofuels from fermentation broth	Poly(vinyl alcohol) Poly(vinylidene fluoride)
	Dehydration of organic solvents	

of materials. Table 1 summarizes some applications of processes based on dense membrane, and the most used polymeric membranes for each application are also reported.

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Density Functional Theory Modeling of Membrane Systems

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Density functional theory is a new methodology in the frame of quantum mechanics (*ab initio*). The assessment of material features depending on the electron interactions or electron density polarization necessarily needs the use of quantum mechanics. Large molecular systems cannot be described with accurate quantum mechanical approaches, such as correlated Hartree-Fock (Szabo and Ostlund 1994), due to the huge computational time required by these. Instead, the density functional theory (Parr and Yang 1989) allows to get results with similar precision in relatively shorter computational time. Thus, density functional theory is a powerful tool to investigate large chemical systems like the nanostructures involved in the membrane preparation. In density functional theory, the total energy of an electronic system is evaluated through a total functional which depends on the electron density of the quantum system, $\rho(r)$, and external potential $v(r)$. It is defined as follows:

$$E_{\text{DFT}}[\rho(r)] = T_s[\rho(r)] + J[\rho(r)] + E_{\text{xc}}[\rho(r)] + \int v(r)\rho(r)dr$$

where $T_s[\rho(r)]$ is the kinetic energy of an isoelectronic noninteracting system, while $J[\rho(r)]$ describes the Coulomb electrostatic energy. The $E_{\text{xc}}[\rho(r)]$ is the exchange and correlation

functional, which takes into account the difference between the kinetic energies of the isoelectronic interacting and noninteracting systems in addition to the difference between the quantum electron-electron and Coulomb electrostatic energy. $\rho(r)$ can be evaluated by the nonlinear Kohn-Sham equations, defined by means of an *effective potential*. The electron density allows to calculate all the properties of the quantum system in addition to the total energy. Computational approaches, based on density functional theory, are applied in the study of catalysts used in membranes and in the study of noncovalent interactions, such as hydrogen-bonding and London dispersion interactions (De Luca et al. 2009). In fact, hydrogen-bonding, electrostatic interactions and London force are important for membranes at the basis of fundamental properties such as molecular adsorption and sorption, recognition, and self-assembly. Also size, shape, and electrostatic features of supramolecular architectures can be studied using density functional theory. All these properties control the selectivity of the materials, used in membranes, the permeability as well as the antifouling or anti-embrittlement features. Density functional theory studies of the catalysis in membrane reactors require the definition of structural models of the catalysts. For the most part, they are modeled by infinite surfaces, slabs, or different types of adsorbed or absorbed atomic clusters. These studies could be treated independently from the aforementioned analysis. However, it is important to emphasize that the merging of the results obtained by the different investigations would be advisable. For example, the kinetic constants characterizing a reaction path, related to a particular catalyst, evaluated by the density functional theory, should be compared with the diffusion coefficients characterizing the permeability of reagents and products through the membrane derived by the adsorption/absorption of different molecules.

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Design of Experiment (DOE)

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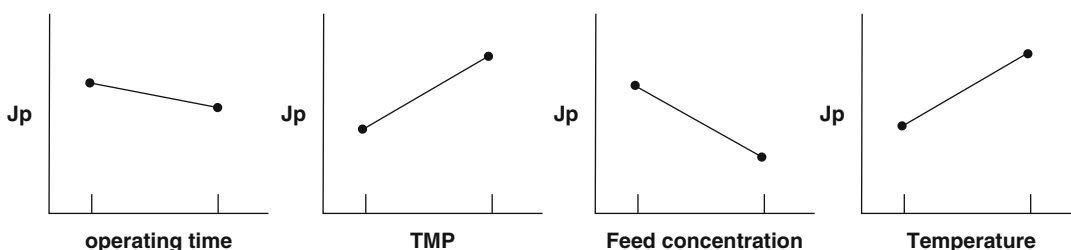
Generally speaking, experiments are performed by investigators in virtually all applications of membrane processes, usually to discover something about a particular process or system. More formally, we can define an experiment as a test or series of tests in which purposeful changes are made to the input variables (also called factors) of a process or system so that we observe and identify the reasons for changes that may be observed in the output response (also called response variables or just response) (Montgomery 2001). Until now the extensively used strategy of experimentation in membrane field has been the one-factor-at-a-time approach. This method consists of selecting a starting point, or baseline set of levels, for each factor, then successively varying each factor over its range with the other factors held constant at the baseline level. After all tests have been performed, a series of graphs are usually constructed showing how

the response variables are affected by varying each factor with all other factors held constant. Figure 1 shows a set of these graphs in which the variation of permeate flux (J_p) is studied as a function of operating time, transmembrane pressure (TMP), feed concentration, and temperature.

Despite that this approach has been widely used, the major disadvantage is that it does not consider any possible interaction between the factors. An interaction is the failure of the one factor to produce the same effect on the response at different levels of another factor. In membrane processes interactions between factors are very common, and if they occur, the one-factor-at-a-time strategy will usually produce poor results. One-factor-at-a-time experiments are always less efficient than other methods based on a statistical approach.

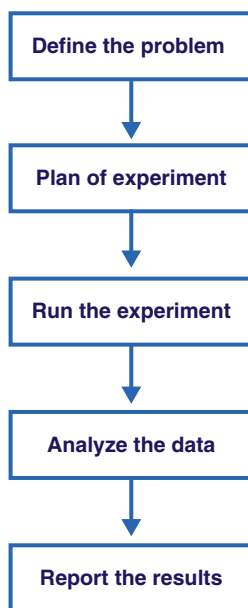
In this regard, DOE can be defined as a systematic approach to understanding how factors affect the response variables such as efficiency, yield, or productivity. DOE uses a statistical methodology to analyze data and predict a response under all possible conditions within the limits selected for the experimental design. In addition, DOE allows to generate the required information in order to determine which factors and interactions are significant in contributing to the response being measured and those factors and interactions that are insignificant and do not contribute to either a particular response. As a matter of fact, the use of this approach allows to save time and money, minimizing the amount of experimentation (Wagner 2014).

DOE includes different classes of designs divided in three main groups such as mixture



Design of Experiment (DOE), Fig. 1 Typical examples of the one-factor-at-a-time strategy concerning the effect of operating parameters on the permeate flux

Design of Experiment (DOE), Fig. 2 Steps involved in design of experiment (DOE)



experiments, screening design, and response surface. Each design is used in specific situations to gather information from a particular set of independent variables. Mixture design can be used to optimize membrane characteristics (response variable) over different compositions of materials, solvents, additives, etc.

On the other hand, screening and response surface designs can be applied to study all the membrane processes, to get the main factors to control and the optimal process conditions, as well. Screening design is used to screen process and/or product variables, while response surface is used to get a better description of their curvature and interactions in the experimental space. Response surface approach, unlike factorial design, includes the quadratic term in the model; therefore it shows curvature.

DOE procedure involves several steps, as shown in Fig. 2.

Defining the problem may seem obvious, but in practice, it is sometimes difficult to do. In this step the aim of the study should be properly and clearly defined before starting any experiment. After the problem is properly defined, the second step in DOE framework is to select independent variables (factors), with their limits for evaluation, as well as dependent variables (responses to

measure for each experiment). The limits used in screening design, as well as response surface, are represented as 1 and -1 for the highest and the lowest value, respectively, and 0 for the middle value.

In membrane processes, some common independent factors include transmembrane pressure, temperature, flow rate, and membrane characteristics as well. On the other hand, permeate flux, rejection, and selectivity are common dependent variables or responses. Independent variables are normally quantitative in nature, meaning that they are set at a specific numerical value. However, in some experimental design, the independent variables are qualitative.

The quantity of experimental runs will depend on the quantity of selected factors as well as the type of design chosen. Experimental design creation produces all possible combinations of maximum, minimum, and middle values. Finally the investigator will obtain the quantity of experimental runs as well as the conditions for each experiment.

The experimental procedure, in which the investigator performs experimental runs according to the experimental design, is a critical step in DOE, because in this phase response variables data are collected for all the experiments or treatment combinations.

Once completed all the experiments and collected all the data for each response variables, data analysis can be performed. Generally the analysis is carried out by using statistic software in which the investigator should:

- Examine the presence of outliers and typos. In this step many graphs such as response distributions (histograms, box plots, etc.) and responses versus factors levels (main effect mean plots and interaction plots), can be constructed.
- Evaluate by means of ANOVA analysis the significance of each factor as well as interaction and quadratic effect (only for response surface designs).
- Create the model to describe the experimental data. The most common empirical models to fit the experimental data take either a linear form

(used in factorial design) or quadratic form (applied for response surface).

- Check the correlation coefficient (R^2) of the model, normal distribution of the residuals (error or noise), and autocorrelation (using Durbin-Watson statistic) as well.

Subsequently, the model can be used to give an answer to the questions fixed in the experiment objectives as well as to determine the optimal conditions to multiple responses.

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Detergents

► Amphiphilic Molecules

Diafiltration

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Diafiltration (also called membrane filtration in dilution mode) is an operation mode of a pressure-driven membrane filtration process in which a diluant (pure solvent) is added into the process liquor in order to facilitate the separation of macrosolutes from microsolute.

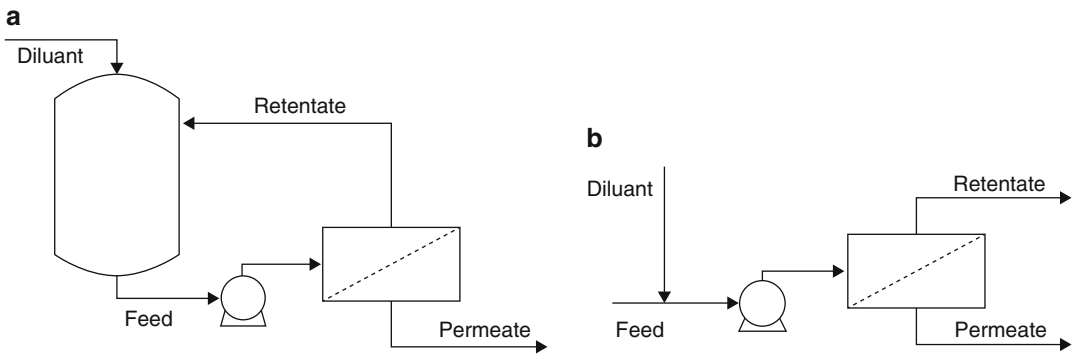
Diafiltration may be performed either in batch (discontinuous) or continuous processing mode as schematically shown in Fig. 1. In both processing modes, diluant is added to and permeate is withdrawn from the system. The fundamental difference between the two configurations is that in

batch operation, the retentate stream is recycled into the feed tank where it is mixed with the content of the reservoir and with fresh diluant. The concentration of membrane-permeable microsolute in the feed tank decreases over time, and the final product is obtained directly in the feed reservoir when operation is terminated. In contrast, continuous processing is performed in a flow-through manner with both permeate and retentate being withdrawn. Thus, batch diafiltration is a dynamic process in which the composition of fluid stream fed into the membrane module is a function of time, while continuous diafiltration is essentially a static (steady-state) process in which the feed stream is of constant composition.

The benefits and disadvantages offered by the two processing modes in industrial-scale ultrafiltration (UF) systems have been summarized by Lipnizki et al. (2002) as shown in Table 1.

Diafiltration has found a vast number of industrial applications in the chemical, pharmaceutical, environmental, biotech, and food and beverage sectors. The requirement for an effective separation is the utilization of a membrane that has a high rejection for macrosolute but allows the passage of microsolute. The mass transport, unlike in dialysis, is driven by pressure differences across the membrane. Depending on the particular application, either the retentate or the permeate is the valuable phase of economic importance (or both), and the applied membrane can be a microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), or reverse osmosis (RO) membrane. Some typical applications include:

- MF: enzyme recovery from fermentation broths; cell harvest and debris removal; separation of casein from serum milk proteins
- UF: protein purification and buffer exchange; ethanol removal from human serum albumin obtained from blood plasma; fruit juice clarification; milk fractionation; Kraft black liquor treatment; recovery of small molecules (e.g., amino acids, antibiotics, organic acids, etc.) from fermentation broth
- NF: desalination of dyes and optical brighteners; partial demineralization of whey; production of desalted and concentrated



Diafiltration, Fig. 1 Schematic flow diagram. (a) Batch diafiltration. (b) Continuous diafiltration

Diafiltration, Table 1 Comparison of batch and continuous diafiltration (Adopted from Lipnizki et al. 2002)

	Batch	Continuous
UF plant investment	Low	High
Batch tank investment	High	Low
Control investment	Low	High
Space requirement UF	Low	High
Space requirement tank	High	Low
Feed volume flexibility	High	Low
Antibiotic/protein concentration in permeate	Variable	Constant
Residence time	High	Low
Temperature flexibility	Low	High
Module efficiency	Low	High
Energy consumption	High	Low

- antibiotics; desalination of gelatin for improved color and whipping properties
- RO: solvent replacement in herb extracts; beer dealcoholization

Diafiltration is also called *membrane filtration in dilution mode* in accordance with the terminology recommendation of the former European Society of Membrane Science and Technology (now known as the European Membrane Society) (Gekas 1988). Although the latter term is less frequently used in the literature, it better reveals that an operation *mode* of a *filtration process* is considered.

Membrane filtration plants are rarely designed exclusively for microsolite removal. Most

applications require a simultaneous microsolite removal (i.e., macrosolute purification) and macrosolute concentration (i.e., feed volume reduction). In many cases, the term *diafiltration* stands for a process that is designed to achieve these dual objectives. In continuous processing, the different modes of operation (i.e., concentration and dilution modes) are assigned to different stages which are connected in series. In batch processing, the targeted twin aims of concentration and fractionation are obtained either in consecutive operational steps (e.g., in traditional diafiltration, intermittent feed diafiltration, sequential dilution diafiltration) or applying specific diluant utilization strategies (e.g., variable-volume diafiltration, dynamic-volume diafiltration). Overall, these characteristics of diafiltration put it in a favorable position in comparison with other separation techniques and even with a sequence of competitive unit operations (Jönsson and Trägårdh 1990).

Cross-References

- [Dynamic-Volume Diafiltration](#)

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In discontinuous diafiltration processes, including both dilution and volume reduction methods, one must specify both the level of volume reduction/dilution in each stage and also the number of stages so the diafiltration factor is not so easily, or meaningfully, defined in those instances.

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Diafiltration Factor

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One of the most commonly used methods of diafiltration is constant volume diafiltration (CVD) also known as continuous diafiltration. In this process, diluant is added to the retentate solution which is undergoing batch ultrafiltration. The process is set up so that the rate of addition of the diluant exactly balances the permeate flow rate – hence the retentate volume is constant. For any given solute with apparent rejection coefficient, σ , the solute concentration declines during a CVD process according to the equation (Cheryan 1998)

$$c = c_0 e^{-(1-\sigma)V_b/V_s}$$

where V_b is the volume of diluant (buffer) added while V_s is the solution (i.e., retentate) volume. The ratio V_b/V_s is termed the diafiltration factor, sometimes referred to as the number of diavolumes. Once the rejection coefficient is known, this quantity completely specifies the reduction in solute concentration that will be achieved during CVD.

Dialysis

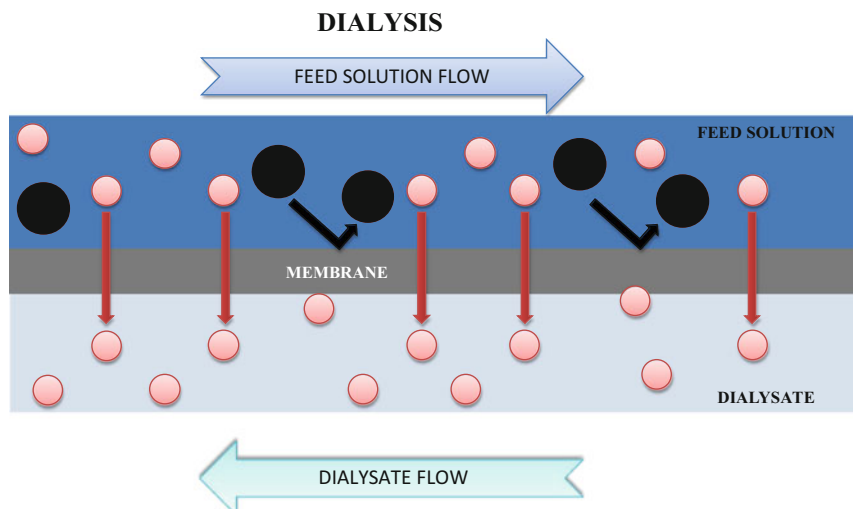
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Dialysis is a process in which small solutes diffuse from a high concentration solution to a low concentration solution across a semipermeable membrane until equilibrium is reached (Strathmann 2006; Mulder 1996). From a liquid solution containing the solvent and molecular components of different molecular weight or sizes (feed solution), the components diffuse through the membrane into the solvent referred as dialysate or “stripping” solution under the force of a concentration difference (Fig. 1). Dialysis process is normally operated in a countercurrent configuration and involves the use of nonporous membrane.

Membrane materials most often used include regenerated cellulose, cellulose acetate, polysulfone, polycarbonate, polyethylene, polyolefin, polypropylene, and polyvinylidene fluoride.

There are different forms of dialysis depending on the components of the feed solution and the structure of the membrane. The most simple form of dialysis is the diffusion of neutral molecules;



Dialysis, Fig. 1 Schematic representation of dialysis process operated in a countercurrent configuration

instead when the electrolytes are separated with neutral membrane or with charged membrane, the process is called Donnan dialysis.

When the feed solution contains neutral molecules, the transport in dialysis is described by the Fick's law:

$$J_i = D_i \frac{dC_i}{dx}$$

where J_i is the rate of transfer of component i or flux, dC_i/dx is the concentration gradient of component i , and D_i is the diffusion coefficient that is a measure of the mobility of the individual molecules.

When feed solution contains an electrolyte which consists of a cation and an anion with significantly different diffusivities, an electrical potential gradient will be created. This potential gradient is referred as diffusion potential, and although it might be very small, it will slow down the faster diffusing ion and speed up the slower ion so that both ions will diffuse with the same velocity. Because the membrane does not carry fixed charges, all ions of the electrolyte are transported in the same direction even if their diffusion coefficient is quite different. In this case, the transport is described by the following equation:

$$J_s = \frac{D_a D_c (z_a + z_c)}{D_a z_a + D_c z_c} \frac{dC_s}{dx}$$

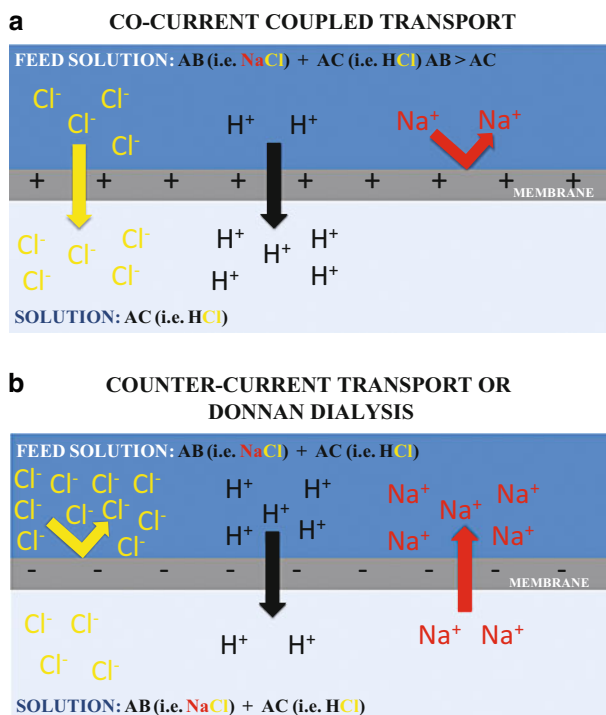
where J_s is the rate of transfer of salts or flux, dC_s/dx is the concentration gradient of salt s , and D_a and D_c are the diffusion coefficients of anion a and cation c , respectively.

The situation becomes more complex if the feed solution contains more than one electrolyte and if the membrane carries fixed charges. There are two forms of coupled transport (Fig. 2):

- Cocurrent or diffusion dialysis (Fig. 2a) when co- and counterions are transported in the same direction
- Countercurrent or Donnan dialysis (Fig. 2b) when no counterions permeate the membrane and co-ion fluxes are in an opposite direction

In the cocurrent coupled transport (Fig. 2a), the feed solution, containing the component A^- (i.e., Cl^-) as anion and B^+ and C^+ (i.e., Na^+ and H^+) as cations, is separated by an anion-exchange membrane, from a solution containing the component A^- as anion and only C^+ as cation. If the concentration of specie AB (i.e., $NaCl$) is assumed to be much higher in the feed solution than in the other solution, while the concentration of AC (i.e., HCl) is supposed to be lower in the feed solution than in

Dialysis, Fig. 2 Schematic diagram illustrating (a) cocurrent coupled and (b) countercurrent transport



D

the other solution, the anion A^- can pass through the membrane from the feed solution to the other solution as a consequence of the concentration gradient. Because of the electroneutrality requirement, an anion can permeate the membrane only when accompanied by a cation. The only cation able to permeate through the membrane by using a specific carrier is C^+ that is transported against their concentration gradient. In the countercurrent coupled transport (Fig. 2b), the feed solution, containing the component A^- (i.e., Cl^-) as anion and B^+ and C^+ (i.e., Na^+ and H^+) as cations, is separated by a cation-exchange membrane, from a solution containing the same components. If the concentration of species CA and BA (i.e., HCl and NaCl) in the feed solution is assumed to be much higher than in the other solution, the anion A^- cannot pass through the membrane, while the cation C^+ moves from feed solution to the other solution and B^+ in the opposite direction against its gradient concentration.

Dialysis process is mainly used to separate low molecular weight components from those of high molecular weight. The major application of dialysis is the artificial kidney; in this application the

blood of a person with a kidney failure is treated in a dialysis process to remove toxic small molecular weight metabolites such as urea, creatine, uric acid, and others. During the treatment, the blood flows on one side of the membrane, whereas dialyzing fluid, which contains vital salts such as sodium, potassium, and calcium that may not be removed from blood, flows on the other side. The small organic solutes diffuse through the membrane, and the process is continued until the concentration of the toxic components has been reduced to a certain level. Other applications are the recovery of caustic soda from colloidal hemicellulose during viscose manufacture and removal of alcohol from beer. Also in biotechnology and pharmaceutical industry, the process is used to remove salts from bioproducts and for fractionation.

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Dielectric Exclusion Model in Membranes

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Introduction

Dielectric exclusion has been recognized in the last two decades as one important mechanism for ion separation in membranes with fixed charges in the active surface as it is the case of NF membranes. They are manufactured to selectively reject a specific ion or ion groups, which was achieved by the inclusion of functional groups (charges) in the membrane active layer. These charges produce an additional rejection due to electrostatic phenomena that hinder the movement of charges through the membrane. Consequently, NF membranes allow the rejection of ions when their size is much lower than the pore size.

The rejection of the target compounds has been studied to occur in two main mechanisms:

- Partitioning mechanisms: steric effect, Donnan equilibrium, and dielectric exclusion; which occur in the interfaces of the active layer.
- Transport mechanisms: convection, diffusion, and electrokinetic effects; which occur through the active layer thickness length.

The phenomenological models available in literature always include the transport mechanisms through the Nernst-Planck simplified equation but not all of them have been implemented with all the partitioning mechanisms recognized year to date. In some cases, dielectric exclusion has been neglected. NF models have four parameters:

1. The ratio (active layer thickness)/(active layer porosity): $\Delta x/A$. It is obtained using Hagen-Poiseuille law.
2. The active layer mean pore radius: r_p . It is usually obtained from experiments of retention

of neutral solutes, atomic force microscopy (AFM), or liquid-liquid porosimetry (Otero et al. 2008).

3. The volumetric charge density: X . It can be inferred by the tangential streaming potential (TSP) technique, where the zeta potential and the surface charge density on the top surface of the membrane are measured and then, assuming that this charge is representative of the selective layer of the membrane, the value of X can be calculated (Martínez et al. 2002). However, a concentration gradient appears through the membrane and X is correlated with this gradient as long as the separation takes place. Thus, a charge gradient has to be considered as well. In a recent work, a Freundlich isotherm was included to correlate X with ion concentration (Silva et al. 2011).
4. Dielectric constant inside the pores: ϵ_p . It can be obtained by impedance spectroscopy technique or by mathematical modeling of designed experiments.

Dielectric Exclusion Model

At the feed and permeate interfaces a thermodynamic equilibrium takes place and a difference of solute concentration (c_i) is generated from one side to the other at each interface. These concentration leaps can be described as:

$$\frac{c_{i,0}}{c_{i,m}} = \phi_i \frac{\gamma_{i,m}}{\gamma_{i,0}} \exp(-z_i \Delta \Psi) \exp(-\Delta W'_{i,B}) \times \exp(-\Delta W'_{i,im}) \quad (1)$$

for the $x = 0$ interface and similarly for the $x = \Delta x$ interface.

In this equation all partitioning effects are included: ϕ_i takes into account the steric effect, the deviation from the ideal bulk solutions at both sides of the membrane is taken into account through the activity coefficients $\gamma_{i,m}$ and $\gamma_{i,0}$; and $\Delta \Psi$ represents the Donnan potential.

The dielectric exclusion is accounted in the terms: $\Delta W'_{i,B}$ for the Born contribution and

$\Delta W'_{i,im}$ for the effect of the image forces (Yaroshchuk 2000). The expressions typically used for these dielectric effects are shown in Box 1.

In the Born effect, a difference between the dielectric constants of the bulk solution (ϵ_b) and the solution inside the pore (ϵ_p) exists as a result of confinement effects. Therefore, to transfer the ions from the bulk solvent to the membrane is necessary to make an extra work that can be estimated using Born equation (Eq. 2) and assuming that ϵ_p must be lower than ϵ_b .

The image force effects appear when two media of different dielectric constants, like a membrane matrix and an electrolyte solution, are in contact and the interaction of ions with the electrical charges induced by the ions at the interfaces causes a dielectric exclusion. The interaction with a polarized interface is well known as “image force” in analogy to the interaction with a fictitious image charge located at the other side of the interface, at the same distance from it than the real charge. The sign and magnitude of the image are determined by the dielectric constants of the media. Consequently, the exclusion due to image force effect depends on the difference between the dielectric constant of the membrane matrix (ϵ_m) and the solution inside the pores.

Equations 1, 2, 3, 4, 5, 6, 7, and 8, have to be introduced the more global a complex NF model for the resolution where ϵ_p appears as only fitting parameter (or coupled with X). A resolution algorithm can be found in specific literature for NF modeling (Yaroshchuk 2000).

Nowadays, all authors are in agreement that dielectric effect must be used to characterize the rejection of ionic solutions. But, there is still controversy if Born or image force effects are more suitable for NF. The Born effect has been used by many authors (Bowen et al. 1997; 2002) neglecting the image force effects, since the small NF pores make the ϵ_p value close to the

one of the membrane, reducing the effect of image forces within the pores while increasing the solvation energy barrier. In that case, Eq. 2 is used as an approximation to obtain the dielectric exclusion effect.

Box 1: Dielectric Exclusion Mathematical Model

The dielectric Born energy ($\Delta W_{i,B}$)

$$\Delta W'_{i,B} = \frac{(z_i e)^2}{8\pi\kappa_B T \epsilon_0 a_s} \left(\frac{1}{\epsilon_p} - \frac{1}{\epsilon_b} \right) \quad (2)$$

Where a_s is the cavity radius defined by Rashin and Honig (Rashin and Honig 1985) as the distance from the center of the ion to the point where the dielectric constant becomes different than the vacuum one, ϵ_0 .

The dielectric image force energy ($\Delta W_{i,im}$)

This effect depends on the geometry of the pores,

$$\Delta W'_{i,im} = \frac{2\alpha_i}{\pi} \int_0^\infty \frac{K_0(k)K_1(v) - \beta K_0(v)K_1(k)}{I_1(v)K_0(k) + \beta I_0(v)K_1(k)} dk \quad (\text{Cylindrical geometry}) \quad (3)$$

$$\Delta W'_{i,im} = -\alpha_i \ln \left[1 - \left(\frac{\epsilon_p - \epsilon_m}{\epsilon_p + \epsilon_m} \right) \exp(-2\mu) \right] \quad (\text{Slit-like geometry}) \quad (4)$$

Where,

$$\alpha_i = \frac{(z_i F)^2}{8\pi\epsilon_0\epsilon_p RT N_A \Gamma_p} \quad (5)$$

$$v = \sqrt{\kappa^2 + \mu^2} \quad (6)$$

$$\mu = Fr_p \sqrt{\sum_i \frac{z_i^2 c_{i,m} \phi_i (\gamma_{i,m}/\gamma_{i,0}) \exp(-z_i \Delta\Psi - \Delta W'_{i,B} - \Delta W'_{i,im})}{RT \epsilon_0 \epsilon_b}} \quad (7)$$

$$\beta = \frac{\kappa}{\sqrt{\kappa^2 + \mu^2}} \left(\frac{\epsilon_m}{\epsilon_p} \right) \quad (8)$$

The K_0 , K_1 , I_0 , I_1 are the modified Bessel functions, ϵ_m is the dielectric constant of the dry polymer of the membrane, which is usually a constant value obtained from bibliography

Cross-References

► Impedance Spectroscopy

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- presence of an applied electric field (Cosgrove 2010; Hunter 2001). The ratio of the dielectric permittivity of a material to that of a vacuum ($\epsilon_o = 8.85 \times 10^{-12}$ F/m) is defined as the dielectric constant (k). Water has a dielectric constant of 80.1 at 20 °C; this large value reflects the highly polar nature of water.
- The dielectric permittivity appears in a number of important equations describing the surface charge and electrostatic interactions in membrane systems. For example, the membrane zeta potential (a measure of the membrane surface charge) can be evaluated from the measured streaming potential (E_z) using the Helmholtz-Smoluchowski equation:

$$\left(\frac{E_z}{\Delta P} \right) = \frac{\epsilon \zeta}{\eta A_o}$$

where ΔP is the pressure difference across the membrane, η is the solution viscosity, ζ is the zeta potential, and A_o is the solution conductivity (Burns and Zydney 2000).

The distance over which the electrical potential varies in an electrolyte solution is described by the Debye length (λ_D), which provides a measure of the thickness of the electrical double layer (Hunter 2001):

$$\lambda_D = \left[\frac{F^2}{\epsilon RT} \sum Z_i^2 C_i \right]^{1/2}$$

where F is Faraday's constant, R is the ideal gas constant, T is the absolute temperature, and z_i and C_i are the valence and concentration, respectively, of each ion in solution.

Dielectric Permittivity

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The dielectric permittivity (ϵ) provides a measure of the ability of a material to be polarized in the

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Dielectric Spectroscopy (DS)

► Impedance Spectroscopy

Differential Scanning Calorimetry in Membrane Characterization

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The differential scanning calorimetry (DSC) is a thermodynamic technique that measures the difference in heat flow between sample and related reference against time or temperature, while programming the sample temperature under specific atmosphere conditions (Haines 1995). The sample is contained in a pan and the reference is the related empty pan. There are two kinds of calorimetric techniques, including:

- Heat flux DSC, where sample and reference are heated in the same furnace and a difference of temperature (ΔT) is measured. Successively, the signal is converted to a power difference by the calorimetric sensitivity.
- Power-compensated DSC, where both the sample and reference are heated in two independent heaters, while the electrical power ($\Delta P = d(\Delta Q/dt)$), requested to maintain close to zero the difference of temperature between sample and reference, is measured in real time.

The energy flux is associated with a transition or reaction and is graphed as a heat flow along the ordinate, while the temperature or time is the abscissa. In DSC curve, the endothermic peak is associated with absorption of power, while the exothermic peak implies release of power from the sample. The verse of the peaks depends on the sign of the heat flow.

DSC allows studying different events, including phase transitions, glass transition, and

Differential Scanning Calorimetry in Membrane Characterization, Table 1 Thermal transitions and related parameters measurable by DSC

Event	Phase transition	Energy sign	Parameter
Fusion	<i>sol</i> → <i>liq</i>	Endothermic	λ , DH
Crystallization	<i>liq</i> → <i>sol</i>	Exothermic	λ , DH
Evaporation	<i>liq</i> → <i>gas</i>	Endothermic	λ , DH
Condensation	<i>gas</i> → <i>liq</i>	Exothermic	λ , DH
Sublimation	<i>sol</i> → <i>gas</i>	Endothermic	λ , DH
Deposition	<i>gas</i> → <i>sol</i>	Exothermic	λ , DH
Glass transition		Change of the baseline	C_p
Chemical reactions		Exothermic/endothermic	DH

chemical reactions. For each thermal event, thermodynamic magnitudes such as latent heat (λ), specific heat (C_p), and/or a variation of enthalpy (ΔH) can be calculated (Table 1).

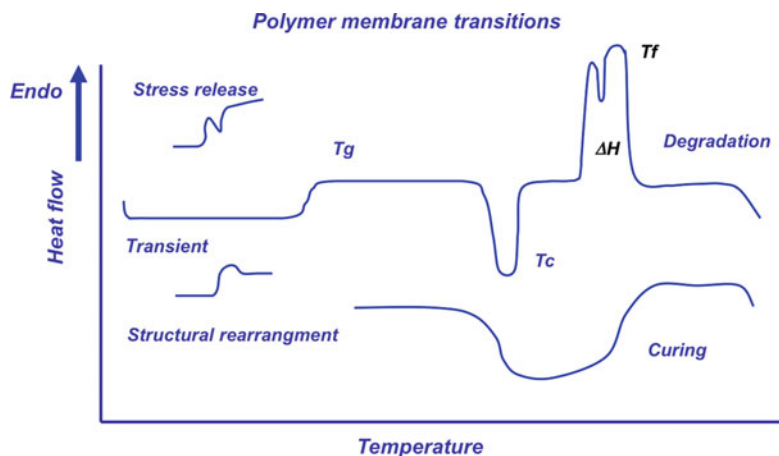
The transitions studied for polymers and compounds at low molecular weight can also be examined for related membranes (Gugliuzza and Drioli 2003). DSC plays a relevant role in materials science and membrane technology, because it permits to identify the best-performing materials through the identification of structure-transport relationships that form the base of the membrane performance (Gugliuzza and Drioli 2004). History, molecular rearrangements, and interactions are some critical issues to be taken in account when a membrane is processed (Yang et al. 2000). In this respect, DSC analysis can provide useful indication about structural features of the samples enabling the design of new interfaces with superior performance in prospect.

Figure 1 shows typical transitions studied on polymeric membranes, including the glass transition (T_g) that is displayed as a change in the baseline due to a variation of C_p of the polymer forming the membrane.

All amorphous polymers exhibit a T_g ; below this temperature value, the membrane becomes glassy owing to the inability of the polymer segments to rotate and rearrange themselves. When the membrane temperature is increased over its T_g , an increase in energy and free volume is observed due to a broader mobility of the chains,

Differential Scanning Calorimetry in Membrane Characterization,

Fig. 1 Main endothermic and exothermic transitions observable by DSC



which enters the polymer in the rubbery region. Heating and cooling rates as well as chain relaxation can affect T_g value and shape, respectively.

The fusion is another endothermic event involving crystalline domains distributed through the membranes. The amount and extent of these ordered regions depends on the chemistry, molecular weight, and thermal history of the samples. Polymorphism and crystalline features of the membranes can be examined in relation to transport properties and mechanical stability as well. If the polymer forming the membrane is available to crystallize, a release of energy is associated with a decrease in heat flow. The study of crystallization is often more useful than fusion, because it allows distinguishing peaks that normally cannot be well visible in melting.

Phase separation, miscibility, and compatibility of polymer binary blends, copolymers, and, more generally, composites are among the most interesting events to examine by DSC (De Lorenzo et al. 2012). In this case, the ability of the materials to interact and distribute themselves in continuous and uniformly interlaced spaces can be evaluated under different experimental conditions. Other interesting indication about the membranes solidity can be achieved from the study of curing, aging, as well as degradation and oxygen stability. All these parameters can significantly affect the membrane transport properties.

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Diffusion Coefficient

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Introduction

The diffusion coefficient (or ► [diffusivity](#)) is a measure of mobility of a species (atom, molecule, or ion), which depends on the frequency with

which a species moves and the size of each movement. The magnitude of diffusion coefficient is governed by the restricting forces of the medium in which diffusion takes place. The diffusion coefficient is typically associated with, but not limited to, ► [Fick's laws](#) of diffusion. It is generally prescribed to a pair of species. For a multicomponent system, it is prescribed for each pair of species in the system, and diffusion in multicomponent systems is described by the Stefan-Maxwell equation. In a binary system either species can be mobile, or one species can be mobile while the other immobile. The example of the latter is diffusion in porous and nonporous membranes. The diffusion coefficient in membrane governs the membrane permeability and selectivity.

Diffusion Coefficient of Liquid in Porous Membrane

In the case of liquids, the effective diffusion coefficient of solute i in membrane (D_{ei}) is related to the ordinary molecular diffusion coefficient (D_i) in liquid by (Seader et al. 2011)

$$D_{ei} = \frac{\varepsilon D_i}{\tau} K_{ri} \quad (1)$$

where ε and τ are membrane porosity and tortuosity, and K_r is the restrictive factor, which depends on the solute diameter (d_m) and the pore diameter (d_p):

$$K_r = \left[1 - \frac{d_m}{d_p} \right]^4, \quad \frac{d_m}{d_p} \leq 1 \quad (2)$$

When $d_m > d_p$, $K_r = 0$ and the solute cannot diffuse through the pore, which is referred to as size exclusion. In the absence of size exclusion and a hydrostatic pressure gradient across the membrane (the example of such process is diffusive dialysis), the selectivity for the separation of solutes i and j is

$$\alpha_{ij} = \frac{D_i K_{ri}}{D_j K_{rj}} \quad (3)$$

► [Molecular diffusivity](#) of solutes in liquid is estimated using well-established correlations (Seader et al. 2011). For large solutes that can be approximated as rigid spheres diffusing at infinite dilution through a stationary solvent, D_i is predicted from the theoretical equation of Stokes-Einstein. On the other hand, the diffusion coefficients of small solutes at infinite dilution are estimated using the empirical equation of Wilke-Chang or more modern Hayduk and Minhas correlations. In the case of dissolved salt, acid, or base, the diffusing entities are ions. In the absence of an electric potential, the infinite-dilution diffusivity of single salts in an aqueous solution is estimated from the Nernst-Haskell equation.

Diffusion Coefficient of Gas in Porous and Microporous Membranes

The diffusion coefficient of gas in porous membranes depends on the mean free path of the gas molecules (λ):

$$\lambda = \frac{3\mu}{2P} \left(\frac{\pi RT}{2M} \right)^{1/2} \quad (4)$$

where μ is the gas viscosity, T is the absolute temperature, R is the universal gas constant, P is the pressure, and M is the molecular weight of the gas. When $d_p/\lambda \ll 1$, i.e., the collisions with pore wall are much more frequent than the collisions with other gas molecules, the transport is dominated by Knudsen diffusion, and the

► [Knudsen diffusion](#) coefficient of species i in a straight cylindrical pore is given by (Seader et al. 2011)

$$D_{Ki} = \frac{d_p}{3} \left(\frac{8RT}{\pi M_i} \right)^{1/2} \quad (5)$$

In the other extreme when $d_p/\lambda \gg 1$, the ordinary molecular diffusion prevails, and the corresponding molecular diffusivity can be estimated using a theoretical equation of Chapman and Enskog or a more practical semiempirical equation of Fuller, Schettler, and Giddings.

When d_p is comparable with λ , the effective diffusion coefficient of solute i is

$$D_{ei} = \frac{\varepsilon}{\tau} \left[\frac{1}{(1/D_i) + (1/D_{Ki})} \right] \quad (6)$$

In microporous membranes ($d_p < 2$ nm) and particularly in ultramicroporous membranes ($d_p < 0.7$ nm), d_m becomes comparable to d_p , and one of the two possible transport mechanisms is the activated Knudsen diffusion, and the corresponding diffusion coefficient is given by (Shelekhin et al. 1995)

$$D_{AKi} = \frac{d_p}{3} \left(\frac{8RT}{\pi M_i} \right)^{1/2} \exp \left(\frac{-\Delta E_i}{RT} \right) \quad (7)$$

where ΔE_i is the activation energy for diffusion of species i , which rapidly increases as d_p approaches to d_m . On the other hand, when $d_p \gg d_m$, ΔE_i approaches to zero and Eq. 7 simplifies to Eq. 5.

The D_{Ki} , D_{ei} , and D_{AKi} (5–7) are generally referred to as D_{gas} , which is related to the permeability coefficient (P_{gas}) by

$$P_{gas} = \frac{D_{gas}}{RT} \quad (8)$$

Consequently, the selectivity for the separation of gases i and j is solely determined by the ratio of the diffusivity coefficients, which varies depending on the pore size of the membrane. If molecular diffusion dominates, the membrane has no selectivity. If Knudsen diffusion dominates, the selectivity is limited to the square root of the ratio of the molecular weights of solutes j and i . On the other hand, if the activated Knudsen diffusion prevails, very high selectivities are possible (Shelekhin et al. 1995).

Diffusion Coefficient in Nonporous Membranes

The transport of species in nonporous membranes is described by ► [solution-diffusion mechanism](#),

in which the ► [permeability coefficient](#) is the product of the diffusion coefficient and the ► [solubility coefficient](#) (S_i):

$$P_i = S_i D_i \quad (9)$$

Consequently, membrane selectivity is a product of the solubility-selectivity (α_s) and the diffusivity-selectivity (α_D), where the latter is the ratio of the diffusion coefficients. The diffusion coefficient along with P_i , and S_i are considered to be the intrinsic property of the membrane material (Kesting and Fritzsche 1993).

Nonporous membranes are generally formed from synthetic organic polymers; they can be also formed from metals. Diffusion in metal membranes is limited to diatomic gases, which first dissociate and dissolve according to ► [Sieverts' Law](#) and then diffuse as individual atoms through the membrane (Burggraaf 1996). In the case of polymer membranes, the solute does not dissociate before dissolving in the membrane. Consequently, the size of diffusing solutes in polymer membranes may vary considerably. In turn, since the diffusion coefficient strongly depends on the molecular weight of solute, the diffusion coefficients in polymer membranes vary by many orders of magnitude. The effect of the molecular weight on the diffusion coefficient is stronger in ► [glassy polymers](#) than in rubbery polymers (Kesting and Fritzsche 1993).

For a given family of polymers, the diffusion coefficient of solute depends on the fractional free volume of polymer (v_f) according to (Baker 2012)

$$D_i = A \exp \left(\frac{B}{v_f} \right) \quad (10)$$

where A and B are adjustable parameters. Despite the fact that v_f in glassy polymers, which ranges from 15 % to 20 %, is greater than that in rubbery polymers (10–15 %), the diffusivity in rubbers is generally greater than that in glasses. The diffusion coefficients in rubbery polymers range from 10^{-13} to 10^{-8} m²/s. The upper values of this range are comparable to those of molecular diffusion in liquids. The diffusion coefficients in glassy

polymers range from 10^{-18} to 10^{-8} m²/s. The upper values are comparable and sometimes exceed those in the rubbery polymers. This is because of some glassy polymers; in particular ► **polymers with intrinsic microporosity (PIMs)** have extraordinary large v_f (up to 35 %) despite a very rigid polymer backbone (Baker 2012). Generally greater diffusivity in rubbery polymers arises from the fact that portions of the polymer chains can freely move due to thermal motions, and segments of the polymer backbone can also rotate around their axis. On the other hand, thermal motion in glasses is limited. Strong interactions between solute and polymer chains may increase the chain mobility. As the concentration of interactive solute increases, membrane plasticization may occur, leading to increase in the diffusion coefficient of solute (Kesting and Fritzsche 1993).

Diffusion in nonporous membranes is an activated process, and consequently, the diffusion coefficient in both glassy and rubbery polymers increases with temperature according to Arrhenius-type relation (Seader et al. 2011):

$$D_i = A_i \exp\left(\frac{-E_i}{RT}\right) \quad (11)$$

where A_i is a pre-exponential constant which depends among other on the nature of the solute and E_i is the activation energy for diffusion of solute i . Eq. 11 is similar to Eq. 7.

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Diffusion Dialysis

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Diffusion dialysis with ion-exchange membranes is mainly used today to recover acids or bases from a mixture with salts. The process is based on the fact that ion-exchange membranes generally show a high permeability for counterions while being more or less impermeable for co-ions. Exceptions are protons and hydroxide ions which can easily permeate both cation- and anion-exchange membranes. The transport mechanism in diffusion dialysis is more complex than in conventional dialysis due to the electrostatic interaction between positive and negative charges and the electroneutrality requirement (Kobuchi et al. 1987). The process and equipment design is very similar to that used in conventional dialysis. In diffusion dialysis, the driving forces for the transport of ions through the ion-exchange membrane are gradients in their chemical potentials only. There is no external electrical potential applied. The principle of the process is illustrated in 1 showing part of a diffusion dialysis stack for the recovery of HCl from a salt mixture. It is composed of anion-exchange membranes forming cells in which in alternating series a feed solution of an HCl/FeCl₂ mixture and a stripping solution of water is introduced. Since anion-exchange membranes are permeable for H⁺, Cl[−] and H⁺ permeate the membranes, while the other cations (Fe²⁺) are retained (Fig. 1).

The mass transport in diffusion dialysis is determined by the transport of ions and can be determined by the respective mass balance equations described in the literature. A typical application of diffusion dialysis is the recovery of acids from spent pickling solutions used in the metal industry. A typical diffusion dialysis plant is shown in the process flow diagram of Fig. 2. A stack with 100–200 cell pairs is operated with

Diffusion Dialysis,

Fig. 1 Schematic drawing illustrating the principle of diffusion dialysis utilizing anion-exchange membranes to recover an acid from a mixture with salts

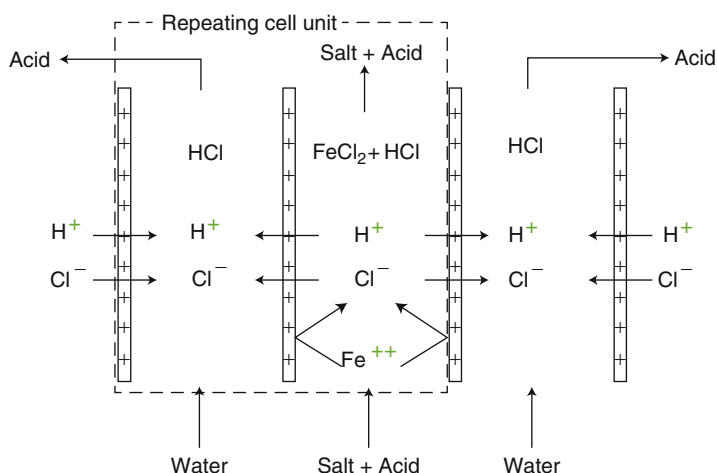
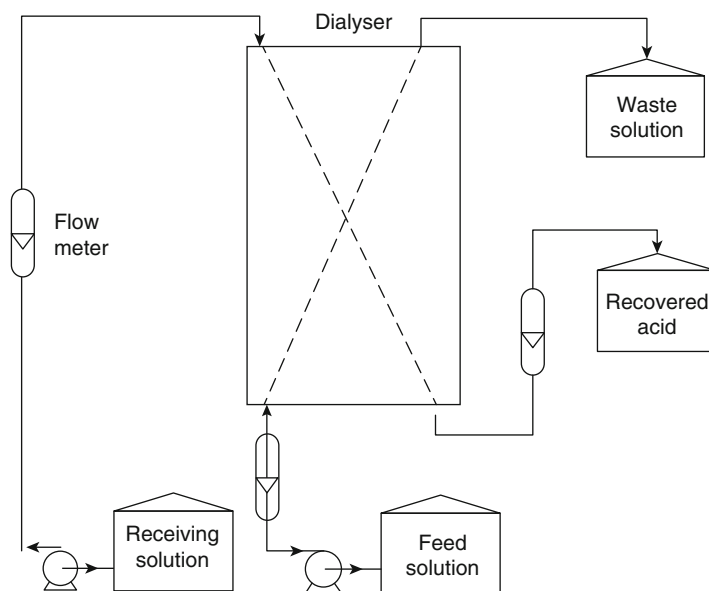
**Diffusion Dialysis,**

Fig. 2 Flow diagram of the diffusion dialysis process



countercurrent flow of the feed and the stripping solutions, which allows high acid recovery rates.

The flow diagram shows a feed solution containing an acid and a salt which often is the effluent of metal surface treatment procedure. This solution is fed by a pump from a reservoir into a dialyser stack which contains only anion-exchange membranes. A stripping solution, which generally is water, is pumped in countercurrent flow into the stack. During the pathway through the stack, the acid diffuses from the feed solution through the anion-exchange membrane into the

stripping solution and leaves the system as salt-free product. The salt is retained and leaves the stack as waste. The main application of diffusion dialysis is in the treatment of spent metal surface pickling solutions (Strathmann 2010; Oh et al. 2000).

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whereas pore flow in meso- and macroporous membranes. Consequently, membrane processes such as gas separation (GS), pervaporation (PV), and reverse osmosis (RO) are governed by diffusion, or more precisely the solution-diffusion mechanism, whereas ultrafiltration (UF) and microfiltration (MF) by the pore flow mechanism.

Diffusion in Membranes

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Introduction

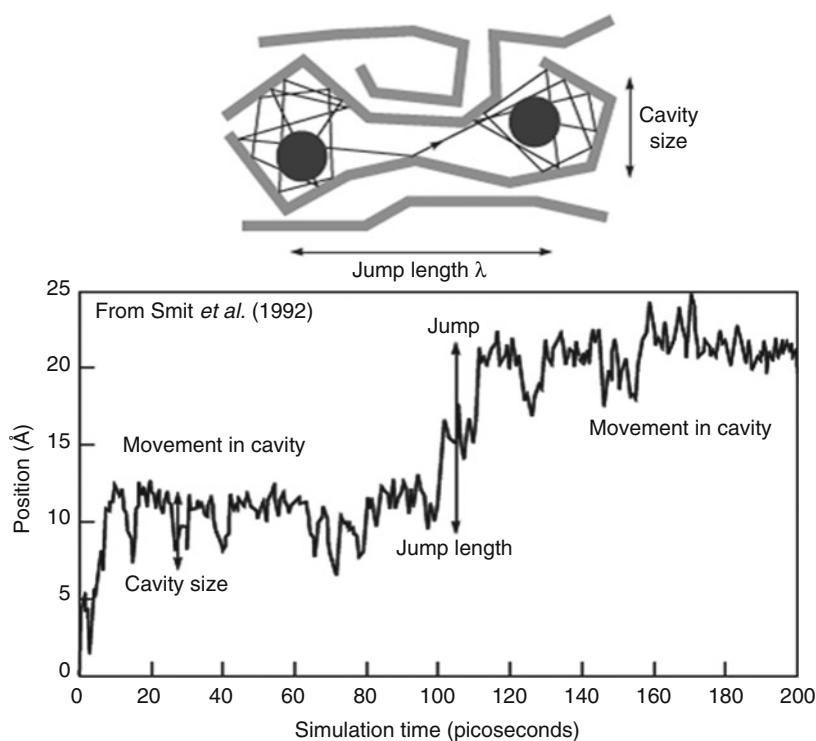
Diffusion is the net movement of a substance (atom, ion, or molecule) from a region of high concentration to a region of low concentration. In the case of membranes, diffusion along with pore flow is the main transport mechanism. Diffusion dominates in dense and microporous membranes

Diffusion in Dense Membranes

Polymeric membranes have generally a dense structure with no visible pores (they are also referred to as nonporous membranes). Molecules permeate through transient free volume elements between polymer chains. A molecule entrapped in a cavity between the polymer chains bounces around the cavity walls and eventually jumps to an adjacent cavity once transient opening for the molecule passage appears. Molecular dynamic simulations, which allow calculations of the fluctuations in the volume between polymer chains due to thermal motion, have been used to visualize diffusion of gases in polymers (Baker 2012). Figure 1

Diffusion in Membranes,

Fig. 1 Motion of a carbon dioxide molecule in a 6FDA-4PDA polymer matrix (Reprinted from Smit et al. (1992). Copyright Elsevier (permission pending))



shows motion of a carbon dioxide molecule in a 6FDA-4PDA polymer matrix. The molecule bounces around the cavity in the first 100 ps and it does not move more than 5 Å, which is indicative of the cavity size. Then, thermal motion moves a segment of the polymer chain allowing the molecule to jump to an adjacent cavity, where it remains until another movement of the polymer chain allows it to jump to another cavity (Baker 2012). The diffusion coefficient (D) in polymer membranes is therefore defined (Koros and Fleming 1993):

$$D = \frac{f\lambda_d^2}{6} \quad (1)$$

where f is the average jump frequency and λ_d is the average jump length. The smaller the molecule the more frequent jumps between the cavities. However, in addition to the size, the shape of the molecule is also very important. For example, carbon dioxide is known to be much more diffusive in polymer membranes than methane even though carbon dioxide has a slightly greater molar volume than methane. On the other hand, methane is a spherical molecule with a kinetic diameter of 3.72 Å, while the molecule of carbon dioxide is an oblate ellipsoid 5.25 Å long, but with the diameter of only 3.03 Å. Consequently, as carbon dioxide molecule bounces around in a cavity it occasionally becomes oriented in such a way that it can jump through a gap between the polymer chains as small as 3.03 Å. Such a small gap would not permit jumping of the methane molecule (Baker 2012).

As temperature increases, the thermal motions of polymer chains allowing the molecule to jump from one cavity to the other become more frequent, and also the molecule bounces faster with a cavity, which means that once a transient opening of appropriate size becomes available, it will more likely jump into the adjacent cavity. Experimentally observed dependence of D in polymeric membranes on temperature follows the Arrhenius relationship (Burggraaf 1996):

$$D = D^* \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (2)$$

where ΔE_a is the activation energy for diffusion, D^* is a preexponential factor often related to the entropy of activation and the average jump length, and R and T are the universal gas constant and the absolute temperature, respectively. Diffusion process in which D follows Eq. 2 is referred to as an activated diffusion. The activation energy for diffusion in polymeric membranes is positive; thus, the greater the ΔE_a the smaller the D ; also it indicates that D increases with T , which is consistent with molecular dynamics simulations. In turn, ΔE_a is directly proportional to a cohesive energy density (CED), which is indicative of strength of attractive forces between adjacent polymer chains. The CED increases when polar and hydrogen bond groups are present in polymer chains (Koros and Fleming 1993).

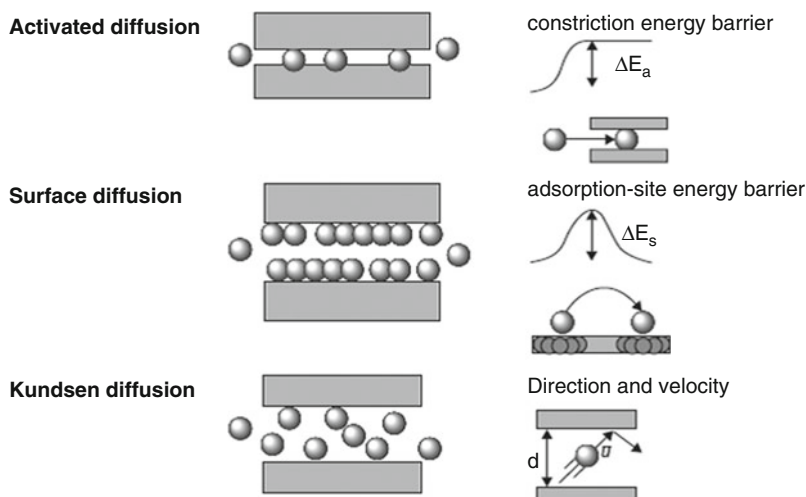
Diffusion in Microporous Membranes

Microporous membranes have permanent pathways (pores) for transport of molecules. They are generally made from inorganic materials such as zeolites, carbonized polymers, and amorphous silica; however, organic membranes made from polymers with intrinsic microporosity (PIM), such as polytrimethylsilylpropyne (PTMSP), are also considered as microporous (Baker 2012).

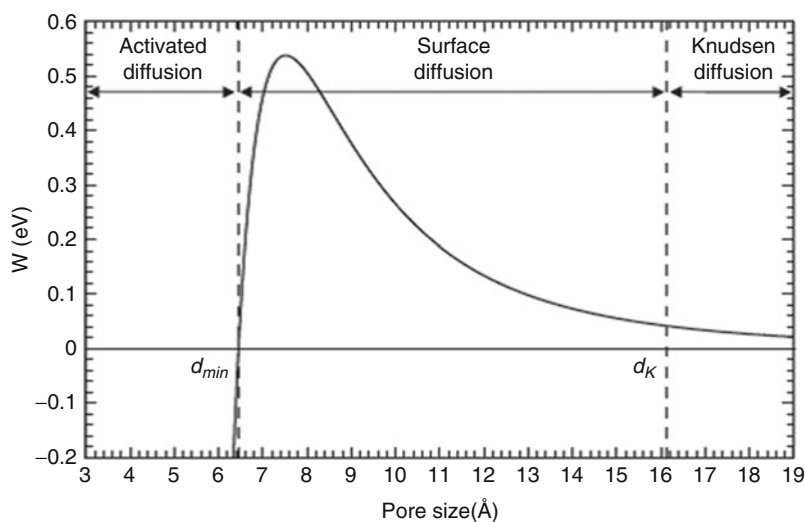
The three most common diffusion mechanisms in microporous membranes, shown in Fig. 2, include activated diffusion (small pores), surface diffusion (intermediate pores), and Knudsen diffusion (large pores). The exact pore size ranges for a given diffusion mechanism are determined based on the difference (W) between the potential energy outside the pore (E_{out}) and the potential energy within the pore (E_{in}) (Thornton et al. 2010).

As a molecule approaches a pore opening, each atom in the gas molecule interacts with every atom from the pore wall through van der Waals forces. The potential difference is also referred to as a suction energy; because a positive W translates to a force sucking the molecule from outside to inside of the pore (adsorption), while a negative W results in a force repulsing the

Diffusion in Membranes,
Fig. 2 Diffusion mechanisms in microporous membranes (Reprinted from Thornton et al. 2010. Copyright John Wiley & Sons. (permission pending))



Diffusion in Membranes,
Fig. 3 Potential energy difference for a single oxygen molecule at the entrance of a carbon cylindrical pore (Reprinted from Thornton et al. 2010. Copyright John Wiley & Sons. (permission pending))



molecule from the pore. The activated transport takes place when $W < 0$, and the activation energy for diffusion in Eq. 2 corresponds to $\Delta E_a = |W|$ (Thornton et al. 2010).

Figure 3 presents an example of the potential energy difference as function of pore size (d) for a single oxygen molecule entering a cylindrical carbon pore from outside environment, in which $E_{\text{out}} = 0$. The pore diameter corresponding to $W = 0$ is referred to as a minimum pore size (d_{min}), while the pore diameter corresponding to $W = RT$ represents Knudsen diameter (d_K). Activated diffusion occurs when $d < d_{\text{min}}$, surface diffusion dominates when $d_{\text{min}} < d < d_K$, while

Knudsen diffusion dominates when $d > d_K$. Table 1 summarizes d_{min} and d_K for different gases in carbon and silica pores with two different pore geometries.

Activated Diffusion Versus Surface Diffusion

When transport is dominated by activated diffusion, there is no adsorption and membrane permeability (P) is solely governed by the diffusion coefficient, i.e.:

Diffusion in Membranes, Table 1 Minimum pore size for the activated transport ($d_{\min}$) and minimum pore size for Knudsen diffusion (d_K) at room temperature (298 K). All pore sizes are given as the PAS pore size^a (Adapted from Thornton et al. 2010)

Gas	Pore geometry							
	Cylindrical pore				Slit-shaped pore			
	Carbon		Silica		Carbon		Silica	
	$d_{\min}$ (Å)	d_K (Å)	$d_{\min}$ (Å)	d_K (Å)	$d_{\min}$ (Å)	d_K (Å)	$d_{\min}$ (Å)	d_K (Å)
He	2.30	5.69	2.53	6.37	1.86	2.19	2.06	4.35
H ₂	2.57	8.82	2.79	9.79	2.10	6.52	2.31	7.22
CO ₂	2.95	12.30	3.17	13.35	2.46	9.27	2.65	10.12
O ₂	3.10	11.68	3.31	12.68	2.59	8.76	2.79	9.58
N ₂	3.27	11.49	3.48	14.46	2.75	8.60	2.94	9.39
CH ₄	3.49	13.74	3.69	14.84	2.95	10.43	3.13	11.32
CO	3.32	12.14	3.52	13.16	2.79	9.14	2.98	10.00
Ar	3.18	11.68	3.39	12.67	2.66	8.76	2.86	9.56
n-C ₅ H ₁₂	5.27	23.51	5.45	25.04	4.59	18.33	4.75	19.57
C ₂ H ₆	4.02	16.69	4.21	17.93	3.44	12.82	3.62	13.86
SF ₆	4.66	19.46	4.85	20.81	4.03	15.05	4.20	16.15

^aPositron annihilation spectroscopy (PAS) diameter $d' = d - \delta d$, where δd is the electron cloud thickness surrounding the surface atoms ($\delta d = 3.32$ Å)

$$P = P^* \exp\left(\frac{-\Delta E_a}{RT}\right) = P^* \exp\left(\frac{-|W|}{RT}\right) \quad (3)$$

where ΔE_a is the activation energy for diffusion, which is identical to ΔE_a in Eq. 2, which is equal to the absolute value of the potential difference. On the other hand, when transport is dominated by surface diffusion, membrane permeability (P_s) is governed by both the diffusion coefficient (D_s) and the solubility coefficient (S_s). The latter is a thermodynamic factor that correlates the concentration of molecules in the adsorbed phase to the external pressure, which typically follow a Langmuir isotherm. At the same time, S_s follows Arrhenius relation:

$$S_s = K_o \exp\left(\frac{q}{RT}\right) \quad (4)$$

where q (>0) is a heat of adsorption, which implies that S_s decreases with temperature. Surface diffusion is an activated process, which depends on q :

$$D_s = D_s^* \exp\left(\frac{-aq}{RT}\right) \quad (5)$$

where a is a proportionality constant ($0 < a < 1$). The product aq is the activation energy for surface

diffusion, which represents the energy barrier separating two adjacent sorption sites (Thornton et al. 2010). Since $P_s = D_s S_s$, combining Eqs. 4 and 5 leads to:

$$P_s = P_s^* \exp\left(\frac{(1-a)q}{RT}\right) \quad (6)$$

The term, $(1-a)q$ is positive; therefore, P_s , unlike P , decreases with temperature. In the case of dense polymeric membranes, the permeability coefficient is also a product of the diffusivity and the solubility coefficients, and the latter, similarly to the surface diffusion solubility coefficient, decreases with temperature. On the other hand, the corresponding increase in diffusivity overcompensates a decrease in solubility. Thus, the permeability coefficient in dense polymeric membranes follows Arrhenius-type relationship similar to the permeability coefficient for activated diffusion in microporous membranes.

The third diffusion mechanism, Knudsen diffusion, is not an activated process. Although Knudsen diffusion coefficient increases with temperature, it does not follow Arrhenius-type relationship (Thornton et al. 2010).

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Diffusive Flow

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Introduction

Diffusive flow (► [diffusive transport](#)) refers to the transfer of matter by diffusion. Quantitative study of diffusive flow dates back to the nineteenth century to the works of Thomas Graham and Adolf Fick. The latter was formulated to what is now known as Fick's first law of diffusion:

$$J = -D \frac{\partial c}{\partial z} \quad (1)$$

where J is the diffusive flux, D is the diffusion coefficient, and c is the concentration of species transported by diffusive flow and z is a coordinate along which the net diffusive transport occurs. The diffusive flow is therefore a concentration gradient-driven process, with the net mass transfer from high concentration to low concentration region. Diffusive flow may occur along with a convective flow. For a binary system (A , B), the

total flux of component A (N) relative to a fixed frame of reference is

$$N_A = J_A + y_A N = J_A + y_A (N_A + N_B) \quad (2)$$

where y_A is a mole fraction of A in the binary mixture at a given point. If component B is stationary ($N_B = 0$), for example, when A is transported across a membrane, then

$$J_A = N_A (1 - y_A) \quad (3)$$

Fick's first law of diffusion is limited to binary systems. Therefore, if diffusive flow of a binary mixture takes place across a membrane, counting the membrane as a stationary component, the system is ternary. For ternary and more generally multicomponent systems, diffusive transport is described by the Stefan-Maxwell equation. Diffusive flow is the main transport mechanism in several membrane separation processes, including ► [gas separation](#), ► [pervaporation](#), reverse osmosis, and diffusive dialysis.

Driving Force for Diffusive Flow

Fick's first law implies that the driving force for diffusion is the concentration gradient. In the simplest example of diffusive flow in membranes – ► [Knudsen diffusion](#), which occurs in porous membranes in which the collisions between gas molecules and pore walls are more frequent than those between the gas molecules – the concentration gradient is expressed in terms of the partial pressure gradient for binary and multicomponent system and as a total pressure gradient for the single gas transport. However, in the more rigorous analysis, the true driving force is the gradient of chemical potential. Assuming applicability of the ideal gas law, a more general expression for the flux of component A is given by Kärger et al. (2012):

$$J_A = u_{AC_A} = -\frac{RT}{f} \frac{d \ln p_A}{d \ln c_A} \frac{dc_A}{dz} \quad (4)$$

where u_A is the flow velocity of component A , f is a friction coefficient, R is the universal gas constant, T is the absolute temperature, and p_A is the partial pressure of component A . The term $d \ln p_A / d \ln c_A$ represents the gradient of the equilibrium isotherm in logarithmic coordinates, which is a thermodynamic correction factor. This term may vary substantially with concentration, but in general, at low concentrations (i.e., when c_A is a linear function of p_A), it approaches unity. Comparison of Eq. 1 with Eq. 4 reveals that

$$D_A = \frac{RT}{f} \frac{d \ln p_A}{d \ln c_A} \quad (5)$$

This expression for the diffusion coefficient arises from the interpretation of the diffusive flow as being driven by the gradient of chemical potential and opposed by frictional forces.

Maxwell-Stefan Equations

The Maxwell-Stefan model was originally developed to describe diffusion in homogeneous gas or liquid phase. It considers the diffusion coefficients as inverse drag coefficients representing the interchange of momentum between the different types of molecules. The general form of the Maxwell-Stefan equation for diffusion in a multicomponent mixture is (Kärger et al. 2012)

$$\frac{c_i}{RT} \frac{\partial \mu_i}{\partial z} = \sum_{j \neq i} \frac{c_i J_j - c_j J_i}{c \mathcal{D}_{ij}} \quad (6)$$

where $J_i = u_i c_i$ is the diffusive flux of the i -th component, $\mathcal{D}_{ij}$ represents the Stefan-Maxwell diffusivities, and c is the total concentration. For an ideal gas, the left-hand side of Eq. 6 reduces to $\partial c_i / \partial z$, so for equimolar counter-diffusion in a binary system

$$J_i = -J_j = -\mathcal{D}_{ij} \frac{\partial c_i}{\partial z} \quad (7)$$

which is identical with the usual Fickian formulation given by Eq. 1. The difference between the Fickian and Maxwell-Stefan diffusion coefficients

is that the later takes into consideration the interactions between components i and j , which in dilute systems are negligible. Consequently, the Fickian and Maxwell-Stefan diffusion coefficients are equivalent in dilute ideal systems. On the other hand, they deviate from each other in concentrated systems. However, Fickian diffusion coefficient is known to be a function of concentration in concentrated systems.

Solution-Diffusion Model

Diffusive flow or diffusion is a rate-limiting step in membrane processes such as gas separation, pervaporation and reverse osmosis, in which the transport is governed by the solution-diffusion model (Baker 2012). In this model, it is assumed that penetrant in feed and in feed-side interface of the membrane and the penetrant in the permeate-side interface and permeate are in instantaneous equilibrium. The corresponding equilibrium constant, which is referred to as distribution coefficient or a solubility coefficient (S), is a thermodynamic factor. The solubility coefficient is constant only at low concentrations where the concentration of penetrant in the membrane is a linear function of its concentration in the fluid phase (e.g., Henry's law is applicable). In this case, the diffusive flux can be expressed in terms of the external driving force, for example (Koros and Fleming 1993),

$$J = SD \frac{(p_f - p_p)}{L} = P \frac{(p_f - p_p)}{L} \quad (8)$$

where $P = SD$ is the permeability coefficient, p_f and p_p are the partial pressures of penetrant at the feed and permeate sides, respectively, and L is the membrane thickness. Equation 8 is applicable for gas permeation; however, similar rate equations can be written for reverse osmosis and pervaporation.

Dual-Mode Sorption

Most of practical membranes are made from glassy polymers in which sorption does not follow

linear isotherm according to Henry's law, but rather the so-called ► [dual-mode sorption](#) in which (Kesting and Fritzsche 1993)

$$c = c_D + c_H = Sp + \frac{c'_H bp}{1 + bp} \quad (9)$$

where c_D is the concentration in the Henry-type sites, c_H is the concentration in the Langmuir sites, b is the hole affinity constant, and c'_H is the hole saturation constant, which is a measure of the sorption capacity of the unrelaxed volume. Equation 9 is essentially the summation of Henry and Langmuir isotherms. The molecules in Langmuir sites are partly or completely immobilized; however, the two populations i.e., those in Henry sites and those in Langmuir sites, are in instantaneous equilibrium. Assuming partial immobilization of molecules in Langmuir sites leads to the dual-mobility model, which accounts for two distinct molecular environments with different diffusion coefficients. Consequently, Fick's first law for dual-mobility model becomes

$$J = -D \frac{\partial c_D}{\partial z} - D_H \frac{\partial c_H}{\partial z} \quad (10)$$

where D and D_H are the diffusion coefficients in Henry and Langmuir sites, respectively. Introducing $F = D_H/D$, which varies from 0 (complete immobilization) to 1 (no immobilization in Langmuir sites), and substituting the expressions for Henry and Langmuir isotherms, Eq. 10 can be rearranged to Kesting and Fritzsche (1993):

$$J = -D \left(1 + \frac{FK}{(1 + \alpha c_D)^2} \right) \frac{\partial c_D}{\partial z} \quad (11)$$

Equations 9, 10, and 11 are applicable to single gas permeating through the glassy polymeric membranes. They are easily extendable to binary and multicomponent systems within the classical Fickian diffusion formalism (Zolondz and Fleming 1992), without resorting to Maxwell-Stefan equations.

However, the Maxwell-Stefan formulation has the important advantage that the rate parameters are simply related to directly measurable

quantities, thus making this approach more suitable for use in the correlation of experimental and predictive models (Kärger et al. 2012). This approach has become quite popular for the analysis of diffusive transport in inorganic adsorbent membranes, in which adsorption is described by, but not limited to, Langmuir isotherm, largely because of the work of Krishna and his associates (Wesselingh and Krishna 2000). Nevertheless, because of its simplicity compared to the Maxwell-Stefan formalism, solution-diffusion model based on Fickian diffusion is still by far the most commonly used approach to analyze diffusive transport in membranes.

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Diffusive Transport

► [Diffusivity](#)

Diffusivity

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Synonyms

[Diffusive transport](#); [Molecular diffusivity](#)

For a species in a homogeneous phase, gas, liquid, or solid, diffusivity can be defined as any material transport driven by concentration difference. Its physical origin lies in the random molecular motion that leads to an overall phenomenon of smoothing concentration gradients: any batch systems originally showing concentration difference for one or more species will eventually be completely mixed if enough time is elapsed. Diffusivity is easily quantified by the diffusivity flux, i.e., by how much a species diffuses per unit area per unit time.

There are various practical situations which for different reasons, both theoretical and practical, have received particular attention and have been investigated in depth. A brief summary is given here (Cussler 1997).

- Molecular diffusivity. In this case, the fluid where the phenomenon is taking is considered unbounded so that there is no physical interaction between the diffusing species and the system boundaries. Moreover, the species are considered to be diluted so that any interaction between the diffusing molecules can also be neglected. This is probably the most studied cases, and many systems can be considered to fall in these categories.
- Diffusivity of strong electrolytes. As before here we considered the system to be unbounded. However, there is an interaction between the diffusing molecules which affects the transport rate and must be taken into account.
- Diffusivity of associating solutes. The solute associates to form aggregates (weak electrolytes or micelle), and again this affects the transport rate.
- Solvation. Solute-solvent interactions cannot be ignored in this case.
- Solute-boundary interactions are important: here we can have diffusion in porous media or composite, diffusion in cylindrical pore (Knudsen or surface or capillary or molecular sieving).

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Digitized Structure Model

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Digital Reconstruction

It is a procedure to represent the internal structure of materials in digital form, usually, binary, in three dimensions using data from microphotographs or other sources of spatial correlation data. It has contributed significantly to the visual comprehension of the internal configuration of porous materials, human tissues, and composite materials. In the case of porous materials, like porous membranes, catalyst supports, rocks, etc., a binary representation in three dimensions assigns the value of 0 (or 1) to the voxels that lie in the void space and the value of 1 (or 0) to the voxels in the complementary space (solid) (Torquato 2002, 2010). In this way, one obtains a fully three-dimensional array of flags (0 or 1) that defines in a discretized form the pore space inside the material. This array can then be utilized in simulations of sorption and transport phenomena (Gelb 2009), typically, diffusion, flow, two-phase flow, and dispersion that are of utmost importance in the design and modeling of membrane materials and membrane separation processes. Raw data for the initiation of the reconstruction procedure can be obtained in various ways. Physical serial sectioning along planes that are normal to a fixed direction has repeatedly been used using special microtomes or surface grinders following impregnation of the void phase with some suitable substance (resin, Wood's metal, etc.). Digitization of the photographs of each and every section of the material provides a set of two-dimensional arrays to be combined in a deterministic fashion into a three-dimensional array that discretizes the working sample of the medium. Computer tomography provides the same type of information in an automated or semiautomated manner and enjoys

Digitized Structure

Model, Fig. 1 Stochastic reconstruction of porous material using the fractional Brownian motion method, showing individual volume elements



D

tremendous use in medicine and some types of porous media, most typically in hydrocarbon reservoirs. More recently, stochastic techniques are attracting the increasing interest of investigators in this area inasmuch as they require a single section only rather than a whole series of sections. Provided that the sample is sufficiently isotropic and homogeneous, one can extract valuable geometric and topological data from the section and reconstruct in three dimensions a discretized form of the material that respects the features that characterize the two-dimensional image of the section (Quiblier 1984; Adler 1992). Such features include various moments of the correlation function, typically porosity and autocorrelation function, but also higher-order moments or lineal-length distribution, chord-length distribution, etc. The latter is succeeded by the simulated annealing technique (Kirkpatrick et al. 1983) that, theoretically, is capable of reproducing three-dimensional descriptions of materials from an arbitrary number of moments of the correlation function at the expense, of course, of heavy requirements in computational time. A simpler procedure that has proven efficient for several types of porous membranes including asymmetric ones is the so-called fractional Brownian motion technique that respects the first two moments of the correlation function and, in addition, offers an

interweaving option that allows three-dimensional reconstruction (Fig. 1) at much greater scale than the correlation length of the structure (Kikkinides and Burganos 2000). For materials that have evolved from powders through some agglomeration or sintering process, ballistic or random placement methods can be used that allow mass transfer between coalescing particles at a controlled fashion so as to reproduce the actual grain-size distribution and porosity or solid fraction. Reconstruction of fiber-type materials can proceed in a similar manner. In the case of porous membranes that contain nanoscale pores, scattering techniques can be used that offer in an implicit manner the autocorrelation function, thus sidestepping the stage of microscopy and the subsequent phase of image analysis for the extraction of two-dimensional features.

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Diluant

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Any diafiltration process involves the replacement of solvent (including undesired impurities) with a liquid of desired composition. This liquid is known as the diluant. For example, in constant volume diafiltration (CVD), also known as continuous diafiltration, diluant is added to a tank of unpurified solution while it undergoes batch ultrafiltration. The rate of diluant addition is set equal to the permeate flow rate, and thus the solution (retentate) volume remains constant. The effect of this process is the gradual replacement of the solvent and any solutes with low rejection coefficients with the diluant. Mathematically, the reduction in concentration of any solute, with rejection coefficient, σ , is given by

$$c = c_0 e^{-(1-\sigma)V_d/V_s}$$

where V_d is the volume of diluant added and V_s is the solution (retentate) volume. The ratio V_d/V_s is known as the diafiltration factor.

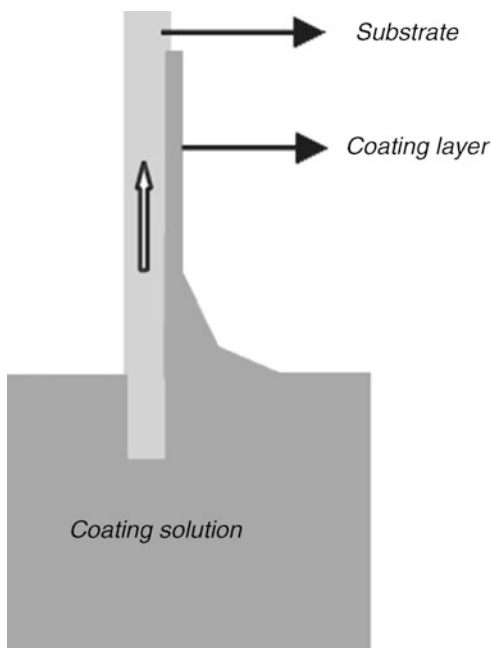
The diluant may be purified water or, more likely, a buffer.

Dip-Coating Method for Ceramic Membrane Preparation

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Dip-coating method for ceramic membrane preparation is one of the most important methods for ceramic membrane preparation. It is usually employed to form the intermediate layer of a ceramic membrane (Lindqvist and Lidén 1997). The procedure is illustrated in Fig. 1 (Li 2007). The drying process starts simultaneously when the substrate is in contact with an atmosphere with a relative humidity below 100 %. In a multiple step process, after calcination of the first layer, the complete cycle of dipping, drying, and calcination is repeated. The raw material is a more



Dip-Coating Method for Ceramic Membrane Preparation, Fig. 1 Dip coating (Li 2007)

interactive powder than the materials used for the support and the porosity is governed by the choice of sintering temperature. The viscosity of the particle suspension and the coating speed or time are the critical factors in dip-coating process (Lindqvist and Lidén 1997). By this method, pore size of the coating layer is possibly smaller than 200 nm, and the process can be conducted continuously (Li 2007).

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Direct Contact Membrane Distillation (DCMD)

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Direct contact membrane distillation (DCMD) is one of the four main possible membrane distillation (MD) configurations. In DCMD process, an aqueous solution colder than the feed aqueous solution is maintained in direct contact with the permeate side of the membrane. Both the feed and permeate aqueous solutions are circulated tangentially to the membrane surfaces (Fig. 1). In this MD mode, the transmembrane temperature difference induces the required water vapor pressure difference between both membrane sides. Consequently, water molecules evaporate at the hot liquid/vapor interface, diffuse in vapor phase through the pores, and are condensed at the

pore-distillate interface on the other side of the membrane at a lower temperature (Fig. 2).

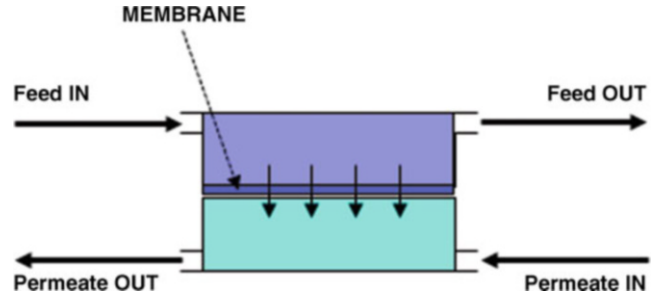
Among the possible MD configurations, DCMD is best suited for applications such as desalination or the concentration of aqueous solutions (orange juice), in which water is the major permeating component. Advantages and drawbacks of DCMD are similar to those of other MD configurations (see Membrane Distillation for a detailed description of benefits and disadvantages of DCMD) and summarized briefly as follows: theoretically 100 % rejection of nonvolatile solutes, lower operating temperature with respect to thermal evaporation processes, and reduced membrane fouling problem with respect to pressure-driven membrane processes, weakly influenced by feed concentration. Therefore, this thermal technique is relatively free from flux reduction by concentrating feed, which is inevitable in the reverse osmosis (RO)-based process. Consequently, the DCMD process is an appropriate alternative for achieving high water recovery from brackish/seawater feeds, managing the concentrate from desalination processes including RO and recovering water from industrial brines.

Heat and mass transfer phenomena occurring in DCMD process are discussed in various recent publications (Lawson and Lloyd 1997; Drioli et al. 2015; Schofield and Fane 1987; Martínez-Díez and Vázquez-González 2000; Gryta et al. 1997; Ali et al. 2013 and see “► Membrane Distillation (MD)”). The flux N can be represented by the following simple correlation:

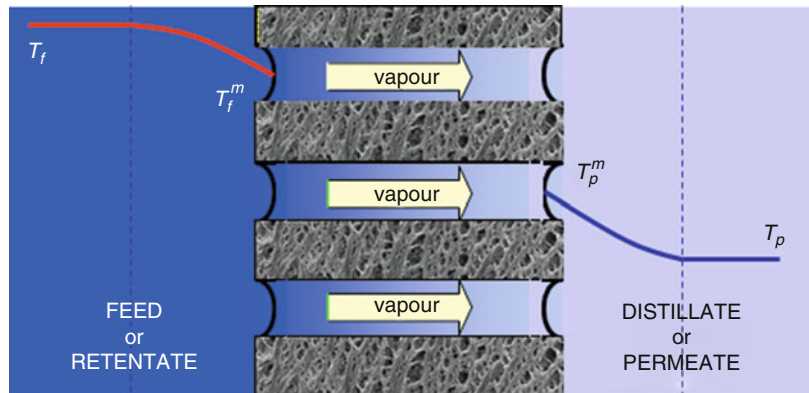
$$N = C(P_{fm} - P_{pm})$$

where C is the membrane characteristic parameter and can be calculated by using various models, depending upon the membrane features and operating temperature applied. $\Delta P = P_{fm} - P_{pm}$ represents the vapor pressure difference across the membrane (function of temperatures and compositions at the membrane surface at feed f and permeate p side, respectively). Mass transfer in direct contact membrane distillation can be separated into three steps (e.g., mass transfer in feed

Direct Contact Membrane Distillation (DCMD), Fig. 1 Typical DCMD schema



Direct Contact Membrane Distillation (DCMD), Fig. 2 DCMD process



boundary layer, mass transfer across the membrane, and mass transfer in permeate boundary layer, as in *membrane distillation*). The mass transfer in permeate boundary layer is not taken into account since the mole fraction of the transporting species in the permeate stream is approximately equal to one. For what concerns the mass transfer in boundary layers, it is general to neglect surface diffusion and viscous flow and to employ a Knudsen-molecular diffusion transition model (Lawson and Lloyd 1997; Srisurichan et al. 2006).

For what concerns heat transfer, the net heat transported through conduction Q_c and due to evaporation Q_v in DCMD can be calculated by using the following relationships (Drioli et al. 2015):

$$Q = Q_c + Q_v = \frac{K_m}{\delta} (T_{fm} - T_{pm}) + J\lambda \quad (1)$$

at steady state

$$Q_f = Q_p \Rightarrow h_f (T_f - T_{fm}) = h_p (T_{pm} - T_p) \quad (2)$$

where Q_f and Q_p represent the heat transferred at bulk feed and permeate side, respectively. Moreover, each h and each T represent the corresponding heat transfer coefficients and temperatures shown in Fig. 2.

The real challenge is to calculate the temperatures at membrane surfaces (T_{fm} and T_{pm}). To realize this, various approaches have been used (Schofield and Fane 1987; Martinez-Diez and Vázquez-González 2000; Gryta et al. 1997). Schofield (Schofield and Fane 1987) suggests the following approach valid when transmembrane surface temperature differences are not greater than 10 °C. In this case the pure water flux can be represented by

$$N = C \frac{dP}{dT} \Big|_{T_m} (T_{fm} - T_{pm}) \quad (3)$$

where $\frac{dP}{dT} \Big|_{T_m}$ can be expressed according to Clausius-Clapeyron equation:

$$\frac{dP}{dT}|_{T_m} = \frac{M\lambda P}{RT^2}|_{T_m} \quad (4)$$

where M is the molar mass of water molecules. Assuming the same temperature polarization on up- and downstream,

$$T_m = \frac{T_f + T_p}{2} \quad (5)$$

Thus Eq. 1 can be written in the following form:

$$Q = \left(\frac{K_m}{\delta} + C \frac{dP}{dT}|_{T_m} \lambda \right) (T_f - T_{fm}) \quad (6)$$

$$Q = H (T_{fm} - T_{pm}). \quad (7)$$

Combining Eqs. 2, 6, and 7

$$(T_{fm} - T_{pm}) = \frac{T_f - T_p}{1 + \frac{H}{h_f} + \frac{H}{h_p}} \quad (8)$$

$$(T_{fm} - T_{pm}) = \theta (T_f - T_p) \quad (9)$$

from Eqs. 3 and 8,

$$\frac{\Delta T}{N\lambda} = \frac{1}{dP/dT} \frac{1}{\lambda C} \left(1 + \frac{K_m/\delta_m}{h} \right) + \frac{1}{h} \quad (10)$$

The permeability C and overall heat transfer coefficient h ($1/h_f + 1/h_p$) can be determined by plotting $\frac{\Delta T}{N\lambda}$ versus $\frac{1}{dP/dT}$ as illustrated by Eq. 10 (Drioli et al. 2015; Schofield and Fane 1987).

Equation 1 was originally developed for $T_{fm} - T_{pm} \leq 10^\circ\text{C}$ and for pure water as feed and permeate. A more general approach for the determination of up- and downstream heat transfer coefficients is based on the use of various empirical correlations. Recently some ambitious attempts have been observed in measuring the membrane surface temperature directly by using different techniques. For example, Ali et al. (2013) have used a cell equipped with 16 temperature sensors to measure the temperature profiles on feed and permeate side in DCMD. The effect of different parameters on thermal

polarization has been investigated by directly monitoring the bulk and interfacial temperatures. The authors have concluded that heat transfer coefficient can be predicted by using the relationship predicted by (Gryta et al. 1997).

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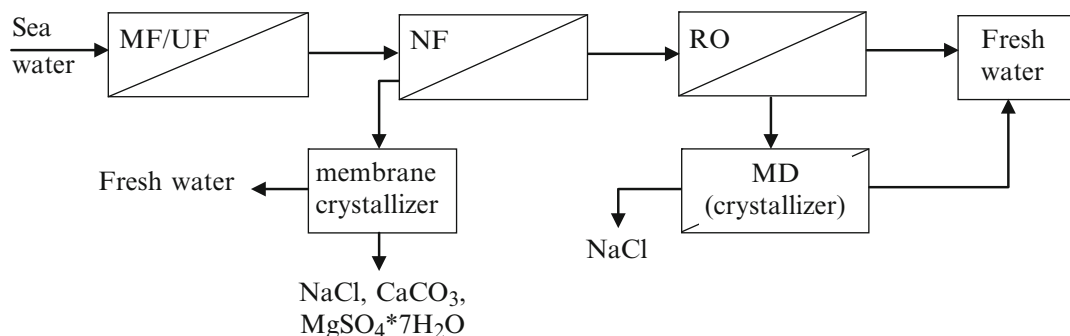
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Direct Contact Membrane Distillation (DCMD) Applications

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DCMD is a membrane distillation (MD) configuration in which both solutions, feed and permeate, are in a direct contact with a hydrophobic porous membrane. Thus, the water vapor transferred across the membrane is directly condensed in a cold permeate inside the membrane module. This configuration has been the most frequently studied due to a simple operation mode in comparison with other MD configurations. DCMD is



Direct Contact Membrane Distillation (DCMD) Applications, Fig. 1 Scheme of sea water desalination plant using integrated membrane system containing membrane

crystallization units operating on the brine from NF and/or RO stages (Based on Di Profio et al. (2010)).

considered as the best choice for applications in which water is the major component of the feeding solution. DCMD can be applied in chemical, food, or pharmaceutical industry and in environmental protection.

The major area of DCMD application is desalination focused on the production of high purity water and freshwater from sea or brackish water. The nature of DCMD driving force causes that nonvolatile solutes such as salts, colloids, and macromolecules that are almost completely retained by a membrane. The permeate is pure water with electrical conductivity of 0.2–2.5 $\mu\text{S}/\text{cm}$, which is suitable for medical, pharmaceutical, or semiconductor industry purposes. Lower temperatures than those usually used in the conventional distillation allow to achieve the permeate fluxes up to 80 $\text{kg}/\text{m}^2\text{h}$ with significant reduction in energy costs. Typical feed temperatures (30–80 $^{\circ}\text{C}$) permit the efficient recycle of low-grade or waste heat streams, as well as the use of alternative energy sources (solar, wind, or geothermal). In addition, the possibility of using plastic equipment also reduces corrosion problems (Drioli et al. 2005; Khayet and Matsuura 2011).

Integration of DCMD with pressure-driven membrane processes such as microfiltration (MF) or reverse osmosis (RO) creates the opportunity for enhancement of water productivity from seawater up to 87.6 %. A development of the system coupling nanofiltration (NF) and RO with DCMD/membrane crystallizer (MCr) might lead to an increase in the total water recovery factor of a desalination plant up to 92.8 %

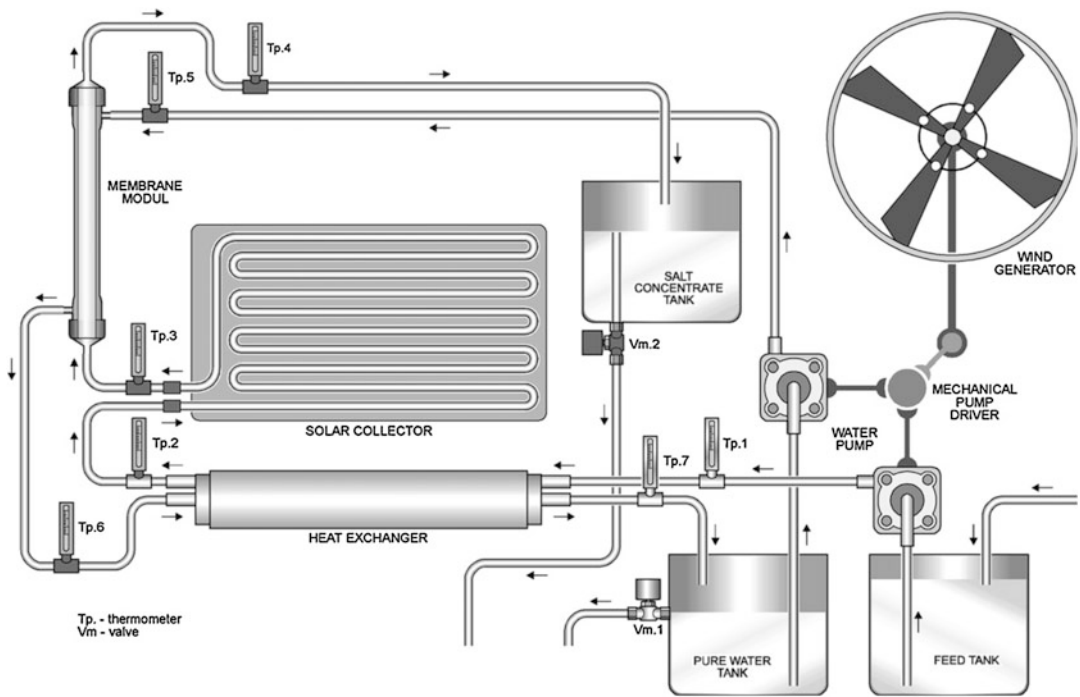
(Fig. 1). An application of the DCMD/MCr system allows to recover both water and salts (commercial products), reducing the environmental problems related to brine disposal (Drioli et al. 2011; Di Profio et al. 2010).

A DCMD system utilizing solar and wind energy for water supply, designed for small board and rural or coastal areas with a lack of electricity, is presented in Fig. 2 (Susanto 2011).

DCMD has also been applied to surface or groundwater treatment. It was found that membrane scaling by CaCO_3 , CaSO_4 , and their mixture occurring in the system can be significantly limited by the feed acidification or antiscalant addition. Moreover, it was found that scaling in DCMD is less severe than in conventional desalination processes (Khayet and Matsuura 2011).

DCMD can be operated with solutions of extremely high concentration of salts, even close to the supersaturated point, and the permeate flux was satisfying. Therefore, DCMD has also been successfully applied to wastewater treatment, either to produce a permeate less hazardous to the environment or to obtain a retentate that contains high concentration of valuable chemicals (Table 1) (Khayet and Matsuura 2011).

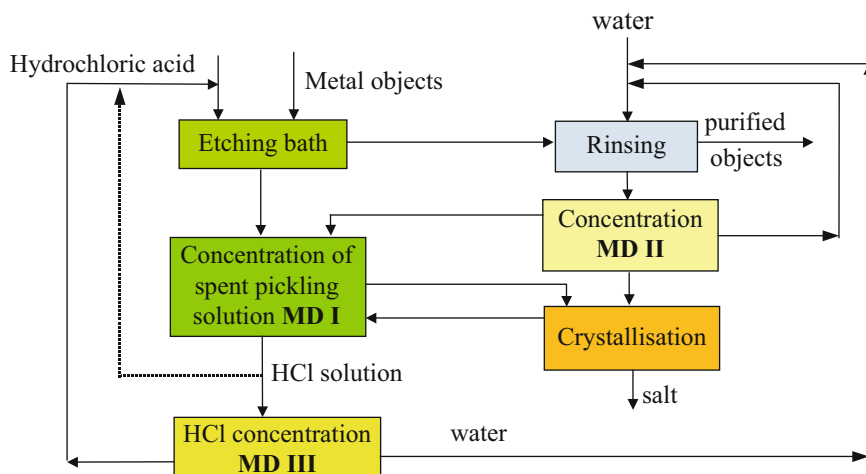
The main disadvantage of DCMD process is a problem with membrane wetting, what limits the concentration of organic compounds to diluted aqueous solutions. The membranes used in MD are chemically resistant; thus, they can tolerate harsh operating conditions. DCMD is a promising method for recovery of HCl from metal pickling



Direct Contact Membrane Distillation (DCMD) Applications, Fig. 2 Schematic diagram of DCMD powered by solar and wind energy (Reprinted from Susanto (2011), copyright (2011), with permission from Elsevier)

Direct Contact Membrane Distillation (DCMD) Applications, Table 1 Examples of DCMD application in various fields

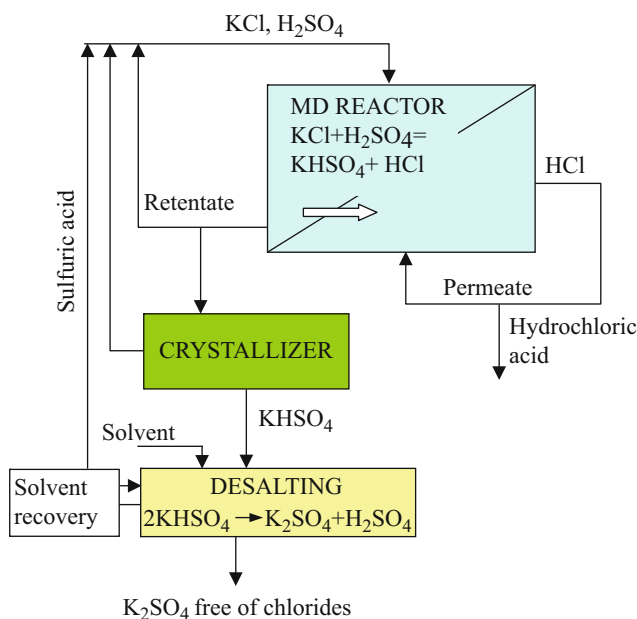
Application area	Examples of application
Water treatment	Desalination of seawater and brackish water, removal of various contaminants (heavy metals, arsenic, boron, humic acid) from surface and groundwater, production of high purity water, removal of low concentrations of organics (ethanol, acetone, acetonitrile, n-butanol)
Wastewater treatment	Treatment of low- and medium-level radioactive wastewater, textile wastewater contaminated with dyes, oil-water emulsions, HCl removal from etching solutions from electrochemical industry, separation of photocatalyst in the photocatalysis-DCMD system, reclamation in space
Medicine and biology	Concentration of an extract of traditional Chinese medicine Concentration of bovine plasma and bovine blood, bovine serum albumin, to ameliorate treatment of uremia
Pharmacy	Pharmaceutical wastewaters containing taurine
Food industry	Concentration of fruit and juices, whey, sugarcane, etc.
Biotechnology	Removal of toxic products from culture broth, production of ethanol in a bioreactor-DCMD system
Chemical industry	Concentration of acids, separation of a half-finished product (HCl) from the reaction mixture to shift the reaction equilibrium in DCMD-chemical reactor system
Other	Ethylene glycol removal from coolant liquids, breaking azeotropic mixtures HCl-water, propionic acid-water, salt crystallization in DCMD/MCr



Direct Contact Membrane Distillation (DCMD) Applications, Fig. 3 The flow – sheet diagram of integrated processes of metal pickling with treatment of spent

solution using DCMD (Reprinted from Tomaszewska et al. 2001, copyright (2001) with permission from Elsevier)

Direct Contact Membrane Distillation (DCMD) Applications, Fig. 4 Scheme of the conversion of potassium chloride into potassium sulfate using integrated system: chemical reactor/DCMD (Based on Tomaszewska and Mientka 2009)



solutions (Fig. 3) (Tomaszewska et al. 2001). The process was also successfully applied in a pilot scale to clean low- and medium-level radioactive waste from a nuclear center.

Moreover, DCMD found success in the treatment of solutions containing substances sensitive to high temperature due to the risk of their degradation, especially in biotechnology and food

industry (fruit juices concentration) (Sotoft et al. 2012).

Novel applications are bio- and chemical reactors integrated with DCMD in which the volatile products are continuously removed from the reaction mixture to shift the equilibrium and improve productivity. It was found that a continuous extraction of ethanol from broth using DCMD

resulted in an increase of its productivity by 87 % (Khayet and Matsuura 2011). The membrane reactor based on DCMD was applied in the production of potassium sulfate for fertilizer industry (Tomaszewska and Mientka 2009). The concentration of the reaction mixture containing KCl and K_2SO_4 close to the saturated state in the membrane reactor resulted in periodical precipitation of $KHSO_4$, whereas HCl was continuously removed from the reaction mixture to shift the equilibrium of the conversion (Fig. 4).

MD is generally recommended for special purposes for which the application of other membrane techniques was considered impossible. Until now the DCMD process has been under development due to high energy consumption and problems with the membrane wettability during long-time operation. However, it should be pointed out that there are numerous calculations showing that DCMD can be economically attractive especially when low-grade energy or alternative energy is used.

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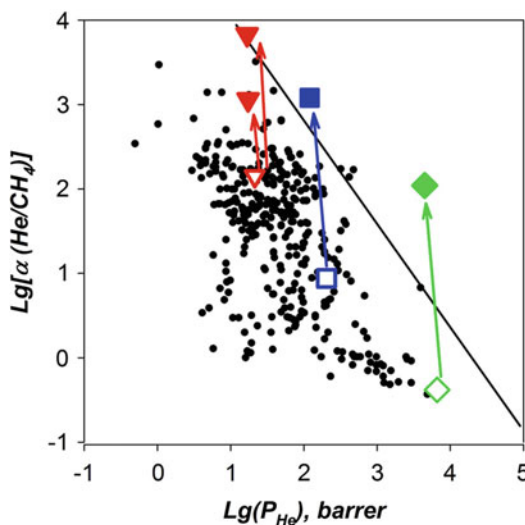
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Direct Fluorination of Polymer Membranes: Gas Separation Properties

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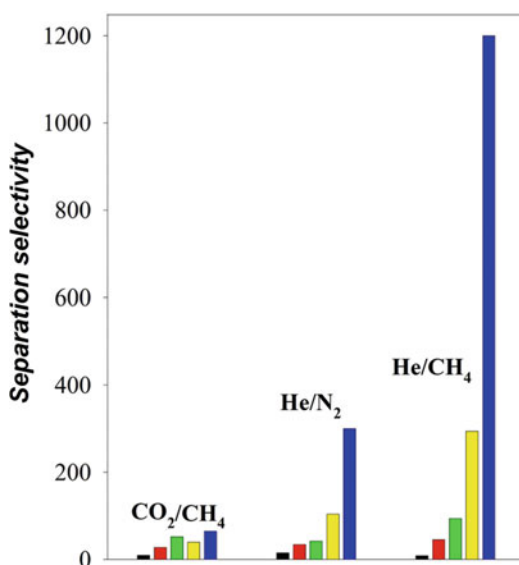
Polymeric membranes can be used for the separation of gas mixtures such as $He-CH_4$, H_2-CH_4 , CO_2-CH_4 , H_2-N_2 , etc. There is, however, a common problem in a gas separation when a polymeric membrane is used: membranes with high gas permeability often have low gas separation factor, and on the contrary, membranes with high separation factor have low permeability (Fig. 1) (Robeson 2008). The direct fluorination can be effectively used to improve gas separation



Direct Fluorination of Polymer Membranes: Gas Separation Properties, Fig. 1 Separation selectivity α for the He/CH_4 mixture vs. permeability of He for various polymer membranes in logarithmic scale. Filled points – literature data (Robeson 2008). Empty triangle, square, and diamond correspond to pristine polyamide Matrimid® 5218 hollow fiber module (points correspond to different treatment conditions) and PVTMS (Kharitonov 2007, 2008) and PTMSP (Langsam et al. 1988) flat membranes. Filled symbols represent transport properties of fluorine treated membranes

properties of polymer membranes when the gas mixture consists of gases with markedly different gas kinetic diameters. In this case substantial increase of separation selectivity (up to several tens times for the case of He/CH₄ mixture) is accompanied with a relatively small decrease (or no change) of permeability of a gas with smaller gas kinetic diameter (He, H₂, etc.). Direct fluorination of polymers is a heterogeneous reaction of gaseous F₂ mixtures with a polymer surface. This is a method of the surface modification: only upper surface layer is modified (~0.01 to several microns in thickness), but the bulk properties (e.g., tensile strength) remain unchanged. The direct fluorination proceeds spontaneously at room temperature with sufficient for industrial applications rate. Fluorination results in a substitution of H-atoms for F-atoms, saturation of double (conjugated) bonds with fluorine, and disruption of majority of C-N and C-Si bonds followed with formation of C-F bonds. The chemical composition of fluorinated layer depends on composition and pressure of fluorinating mixture and treatment duration. Treatment at mild fluorination conditions does not cause disruption of C-C bonds in the main polymer chain. Direct fluorination is a dry technology. Polymer hollow fibers, fabricated membrane modules, and composite membranes can be treated. For the case of hollow fibers and composite membranes, only the dense separation layer can be fluorinated and the porous support will remain untouched, so the tensile strength of membrane element will not be decreased. There are safe and reliable methods to neutralize (by converting into the solid phase) unused F₂ and the end product HF.

The direct fluorination was used to enhance gas separation properties of several polymer membranes (both homogeneous and composite) and hollow fiber modules: polyimide (PI), polyvinyltrimethylsilane (PVTMS), poly(1-trimethylsilylpropyne) (PTMSP), poly(phenylene oxide), polysulfone, poly(4-methylpentene), polycarbonatesiloxane, etc. (Langsam et al. 1988; Le Roux et al. 1994; Amirkhanov et al. 1998; Kharitonov 2007, 2008). Figure 1 illustrates the influence of direct fluorination on separation selectivity for He/CH₄ mixture. As it is



Direct Fluorination of Polymer Membranes: Gas Separation Properties, Fig. 2 Influence of treatment conditions of PVTMS flat membrane on the separation selectivity of CO₂/CH₄, He/N₂, and He/CH₄ mixtures. Treatment condition (from left to right in each group at the plot): virgin PVTMS, treatment with 2 % F₂ + 98 % He mixture, treatment with 33 % F₂ + 67 % He mixture, treatment with 2 % F₂ + 98 % He mixture followed by a grafting of acrylonitrile, treatment with 60 % F₂ + 40 % O₂ mixture

evidenced by Fig. 1, direct fluorination results in a very remarkable increase (by a factor of several tens times or more than hundred times) of separation selectivity. The permeability of He and H₂ is not practically changed after fluorination. Hence the direct fluorination of PVTMS and polyimide Matrimid 5218 provides the possibility to “overjump” the Robeson boundary (straight line in Fig. 1). The direct fluorination can substantially improve the separation selectivity of CO₂/CH₄, He/N₂ and He/CH₄ mixtures (Fig. 2).

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Direct Membrane Emulsification

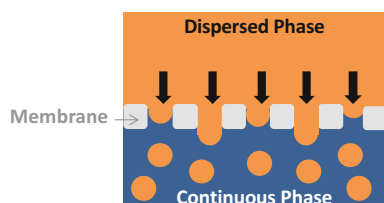
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In the early 1990s, Nakashima and Shimizu (1991) introduced membrane technology for emulsion preparation by the *direct emulsification method* (DME). In DME, the dispersed phase is directly fed through the membrane pores and emulsion droplet formation takes place on the other side of the membrane, which is in contact with the continuous phase (Fig. 1). Here, droplets can detach after reaching a critical dimension either for spontaneous deformation (*Static*



Direct Membrane Emulsification, Fig. 1 Direct membrane emulsification method

Membrane Emulsification), or as a consequence of the shear stress generated by moving the membrane or the continuous phase (*Dynamic Membrane Emulsification*).

Usually, in the DME method, the membrane is wetted by the continuous phase, and hydrophilic and hydrophobic membranes are used in the preparation of oil-in-water (O/W) and water-in-oil (W/O) emulsions, respectively. The mean emulsion droplet size is controlled by the appropriate selection of the pore size of the membrane, and a factor of 2–10 is found between pore size and droplets size. Additional parameters have to be considered to tune the production of an emulsion by DME:

- Shear stress. Uniform and small droplets are obtained when the shear stress increases as a consequence of their faster detachment at the membrane pore surface. In general, the mean droplet size decreases exponentially until it reaches a size where it becomes, more or less, independent of the applied shear. The shear stress can be produced: (i) by flowing the continuous phase tangentially to the membrane surface (cross-flow ME), (ii) by pulsating the continuous phase in the lumen side of the membrane (pulsed ME or pulsed back-and-forward ME), (iii) by rotating or vibrating the membrane, and (iv) by inducing azimuthal oscillation of a tubular membrane.
- Transmembrane pressure. The transmembrane pressure needs to be higher than a critical pressure (capillary pressure) in order to initiate dispersed phase intrusion in the pores. The dispersed phase flux increases with an increase of the transmembrane pressure as more pores are gradually activated for droplet production and the velocity increases in the pores. Larger droplets are produced at higher dispersed phase flux.
- Emulsifier. Droplet size decreases with lower interfacial tension and, according to the time needed by the emulsifier, is dissolved in the dispersed phase to cover the forming droplet surface area. Smaller droplets are produced because of a faster decrease of retaining forces and a reduction of coalescence between the forming droplets at adjacent pores.

One of the main limitations of DME is the low dispersed phase flux through conventional matrix-type membranes (like SPG or ceramic membranes) which have high thickness and tortuous pore channels giving relatively high flow resistance. As an alternative, higher dispersed phase flux at low transmembrane pressure can be achieved using microsieve-type membranes due to their low thickness and well-defined rectilinear pores. Another problem encountered when the amount of the dispersed phase emulsified is increased is the recirculation of the continuous phase (including emulsion drops), giving rise to poor control over the droplet size distribution. This is due to the interactions of the newly forming droplets with droplets in the emulsion, as well as droplet breakup within the circuit. To overcome this problem, advanced methods for dynamic membrane emulsification like rotating, vibrating, azimuthally oscillating membrane emulsification, and pulsed flow have received much attention.

The DME method is suitable for the preparation of simple and multiple emulsions as well as polymeric particles. In the latter case, polymerization, gelation, or coacervation processes of the formed droplets are carried out subsequently to droplet generation.

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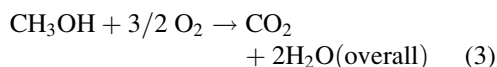
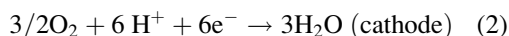
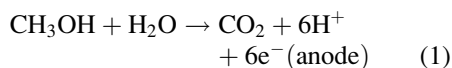
Direct Methanol Fuel Cell (DMFC)

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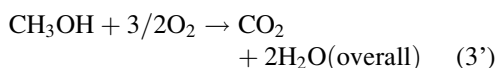
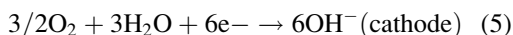
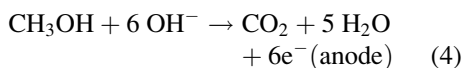
The core of a direct methanol fuel cell is a polymer electrolyte ion-exchange membrane. The electrodes (anode and cathode) are in intimate contact with the membrane faces. A scanning electron

micrograph of a DMFC MEA is shown in Fig. 1 (Aricò et al. 2001). The electrodes usually consist of three layers: catalytic layer, diffusion layer, and backing layer. The catalytic layer is composed of a mixture of catalyst and ionomer, and it is characterized by a mixed electronic-ionic conductivity. The catalysts are often based on carbon-supported or carbon-unsupported PtRu and Pt materials at the anode and cathode, respectively. The membrane as well as the ionomer consists, in most cases, of a perfluorosulfonic acid polymer. The package formed by electrodes and membrane is called “membrane and electrode assembly” (MEA). The overall thickness of this package is generally smaller than 1 mm. Each MEA forms a cell. Several cells are usually connected in series to form a fuel cell stack that is integrated in a system which contains the auxiliaries allowing stack operation and delivering of the electrical power to the external load.

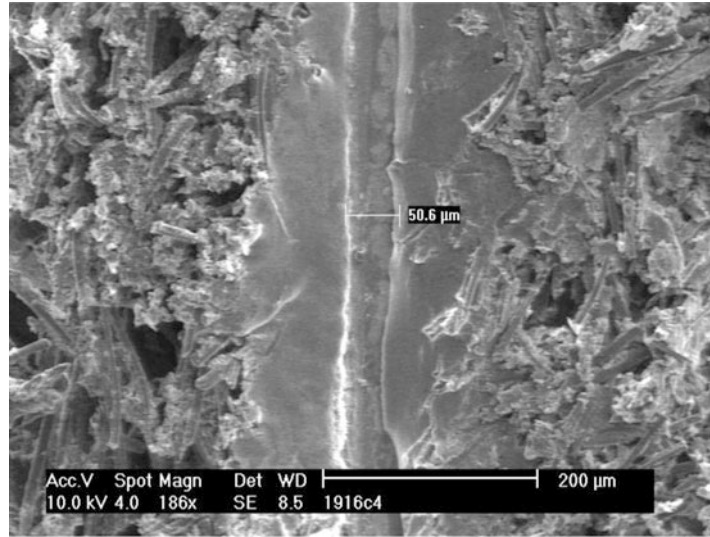
Typical perfluorosulfonic acid membranes used in the present DMFCs, such as Nafion (DuPont), are permeable to methanol transport (Ren et al. 1996), thereby reducing significantly the fuel utilization efficiency of the device. A scheme of the overall reaction process occurring in a DMFC equipped with a proton-conducting electrolyte is outlined below:



In the presence of an alkaline electrolyte, the process is outlined as follows:

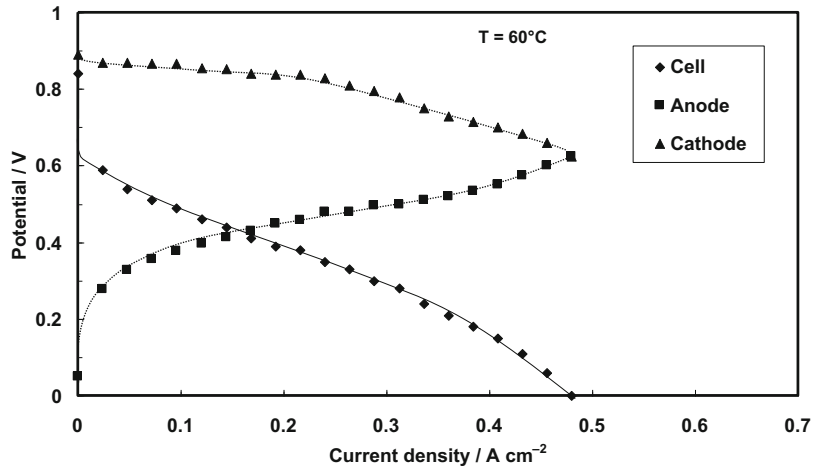


Direct Methanol Fuel Cell (DMFC), Fig. 1 SEM micrograph of a DMFC membrane and electrode assembly equipped with Nafion 112 membrane



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Direct Methanol Fuel Cell (DMFC), Fig. 2 Single-cell and in situ half-cell electrode polarizations for a DMFC operating at 60 °C, ambient pressure, with 1 M methanol at the anode and air feed at the cathode



The thermodynamic efficiency of the process is given by the ratio between the Gibbs free energy, i.e., the maximum value of electrical work (ΔG°) that can be obtained, and the total available energy for the process, i.e., the enthalpy (ΔH°). Under standard conditions:

$$\eta_{\text{rev}} = \Delta G^\circ / \Delta H^\circ; \text{ reversible energy efficiency} \quad (6)$$

with

$$\Delta G^\circ = \Delta H^\circ - (T \cdot \Delta S^\circ) \quad (7)$$

and

$$\Delta G^\circ = -nF \cdot \Delta E_{\text{rev}} \quad (8)$$

ΔE_{rev} is the electromotive force. At 25 °C and 1 atm and with pure oxygen feed, the reversible potential for methanol oxidation is 1.18 V (Aricò et al. 2001). It does not vary significantly in the operating range 20–130 °C and 1–3 bar abs. pressure.

Usually, the open-circuit voltage of a polymer electrolyte direct methanol fuel cell is significantly lower than the thermodynamic or reversible potential for the overall process (Fig. 2). This is mainly due to methanol crossover that causes a mixed potential at the cathode and to the

irreversible adsorption of intermediate species at electrode potentials close to the reversible potential. Direct methanol fuel cells find application in portable power sources, assisted power units (APU), and electrotraction (Dillon et al. 2004).

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Discontinuous Diafiltration by Sequential Dilution (Sequential Dilution Diafiltration)

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Discontinuous diafiltration by the sequential dilution method can be summarized in terms of the three steps shown below. The apparent rejection coefficients are assumed to be 1.0 and 0 for macrosolute and microsolite, respectively.

Step 1: Add buffer to increase solution volume from V_0 to V_f . *Macrosolute (A) and microsolite (B) concentrations decrease.*

Step 2: Use batch ultrafiltration to reduce solution volume back from V_f back to V_0 . *Macrosolute concentration returns to its initial value, microsolite concentration remains unchanged. (This follows from the rejection coefficients of both solutes.)*

Step 3: Repeat steps 1 and 2 as required.

A microsolite balance on the first step gives

$$\beta = c_{B0}/c_{Bf} = V_f/V_0$$

Extending this analysis to n stages (i.e., repeating steps 1 and 2 above n times) gives

$$V_f/V_0 = \beta^{1/n}$$

For example, if the microsolite concentration is to be reduced by a factor of 10 ($= \beta$) and then if a single stage is used, $V_f/V_0 = 10$, while if three stages are used, $V_f/V_0 = 10^{1/3} = 2.15$.

The total volume of buffer used in this case is given by

$$\begin{aligned} V_b/V_0 &= n(V_f - V_0)/V_0 = n(V_f/V_0 - 1) \\ &= n(\beta^{1/n} - 1) \end{aligned}$$

For a single stage system, this ratio works out as 9, while for a three-stage system, it works out as 3.46. Thus, the more stages that are used, the smaller the buffer consumption.

Discontinuous Diafiltration by Volume Reduction (Intermittent Feed Diafiltration)

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The steps involved in a discontinuous diafiltration by volume reduction ([► intermittent feed diafiltration](#)) are outlined below. The apparent rejection coefficient of the macrosolute is 1.0, while that of the microsolite is zero.

Step 1: Batch ultrafiltration from volume V_0 to V_f . *Macrosolute concentration increases, microsolite concentration remains the same because it has a rejection coefficient of zero.*

Step 2: Replace lost permeate with diluant (pure water or buffer). *Macrosolute concentration returns to initial concentration, microsolite concentration reduced.*

Step 3: Repeat steps 1 and 2 as required.

Consider a single “stage,” i.e., steps 1 and 2 above. The concentration of the macrosolute remains unchanged. A mass balance on the microsolute gives the following expression for its concentration at the end of the two-step process.

$$\beta = c_{B0}/c_{Bf} = V_f/V_0$$

If this is repeated n times, one gets

$$V_0/V_f = \beta^{1/n}$$

The buffer consumption is given by

$$\begin{aligned} V_b/V_0 &= n(V_0 - V_f)/V_0 = n(1 - V_f/V_0) \\ &= n(1 - \beta^{-1/n}) \end{aligned}$$

Thus, for a tenfold reduction in microsolute concentration and a three-stage process, one gets $V_0/V_f = 10^{1/3} = 2.15$ in each step, while the buffer consumption works out as $V_b/V_0 = 3(1 - 10^{-1/3}) = 1.607$.

If one stage had been used, one would have had $V_0/V_f = 10$ and $V_b/V_0 = 1.0(1 - 10^{-1}) = 0.9$. Thus, increasing the number of stages increases the amount of buffer required.

The single-stage approach is not always possible as too large a [volume concentration factor](#) (V_0/V_f) might lead to unsustainably high solution viscosities.

Dissolved Oxygen (DO) in Water by Membrane Operations, Removal of

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Dissolved oxygen (DO) is one of the principal components which should be removed for the production of ultrapure water. Even though concentration of DO in water is very low

(approximately 8 ppm under ambient conditions), DO leads to oxidation of dissolved components and materials, for example, boiler piping in (nuclear) power plants. In such systems, the desired DO concentration in the boiler feed water is 7–10 ppb. Therefore, DO removal from water presents a challenging problem for various industries such as production of semiconductors, power plants, pharmaceuticals, and biotechnology. In the production of semiconductors, standard DO level in ultrapure water is the most stringent (below 1 ppb). Removal of DO from water by membrane technology can be accomplished by using gas-liquid *membrane contactors* and *membrane reactors*.

Gas-liquid membrane contactors generally incorporate a porous hollow fiber membrane for direct contacting of two immiscible phases, namely, a gas and a liquid, for the purpose of absorption or stripping without dispersion of one phase into another. The DO removal from water on a membrane contactor requires generation of a driving force for oxygen transmembrane transfer, and this process demands reduction in oxygen concentration in a gas phase. This goal can be accomplished in one of three ways: (1) by applying vacuum to the water, (2) by supplying an appropriate sweep gas to the gas side, and (3) by a combination of the first two where a small flow of sweep gas is used to improve separation driving force but the gas side is still maintained under vacuum (Sengupta et al. 1998). In industrial (commercial) Liqui-Cel[®] gas-liquid membrane contactors, polypropylene porous hollow fiber membranes are used. These membrane contactors offer a serious alternative to the traditional two-stage vacuum degassing towers in the high-purity water treatment systems in the semiconductor industry.

DO removal from water can be performed on a membrane-UV reactor because DO can react with hydrogen to yield water under the action of UV irradiation with a wavelength of 185 nm. This reaction requires dissolution of hydrogen in water, and this process is provided by gas-liquid membrane contactors based on hollow fiber membranes which are permeable for hydrogen and UV irradiation (Li and Tan 2001).

Most efficient existing methods for deep removal of DO from water are based on the principle of oxygen reduction by hydrogen on a palladium catalyst which yields water. The existing catalytic processes for water deoxygenation via hydrogenation reaction involve two stages: (1) absorption of hydrogen in water and (2) passage through a fixed-bed catalytic reactor. In contrast to existing processes, the DO removal on a catalytic membrane reactor can be accomplished in one stage. There are two configurations of catalytic membrane reactors. The first design of the membrane reactor is based on a polypropylene porous hollow fiber membrane module packed with a palladium catalyst, namely, spherical beds of palladium-deposited granules of anion-exchange resin in the void space of the shell side (Li et al. 1995). An alternative design of a catalytic membrane reactor provides *water deoxygenation by catalytic membranes*, namely, by *palladium-loaded hollow fibers* (Volkov et al. 2009). Water and hydrogen are supplied into a shell side of the reactor and into a fiber lumen, respectively. Hence, DO removal is accomplished by chemical reaction between dissolved oxygen and dissolved hydrogen in the presence of the palladium-based catalyst. Using a catalytic membrane reactor, concentration of DO in water of ten parts per billion (ppb) and lower is feasible.

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Distributor Reactor

► Membrane Distributor

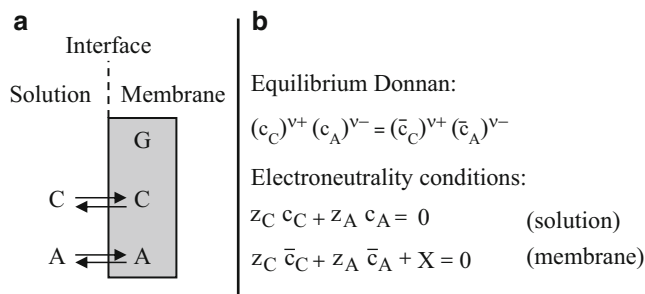
Donnan Effect

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The Donnan effect (which is named after the British chemist Frederick George Donnan (Donnan 1911, 1995) is related to the presence of impermeant ions (i.e., ions that are unable to pass through a semipermeable membrane or boundary) upon one side of a boundary on the distribution of permeant ions across the boundary. At equilibrium, the co-ions (i.e., ions with the same charge polarity as the impermeant ions) will be less concentrated on the impermeant ions' side of the boundary than the other side, whereas the counterions (i.e., ions having the charge polarity opposite to that of the impermeant ions) will be more concentrated there. It results an unequal distribution of permeant ions between the two sides of the boundary.

The surface charged groups (e.g., sulfonic or carboxylic acids) of a synthetic membrane are an example of impermeant ions. When such a membrane is placed in a salt solution, a Donnan equilibrium sets up at both membrane-external solution interfaces. Because of the presence of the membrane fixed charge, the ion concentrations in the membrane are not equal to those in the solution: the concentration of co-ions is lower in the membrane phase than in the solution, while the concentration of counterions is higher there. A potential difference, called the Donnan potential, is created at the membrane-solution interface to counteract the transport of the co-ions to the membrane phase and the transport of counterions to the solution. In other words, the co-ions are repelled by the membrane, whereas the counterions are attracted.



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Donnan Effect, Fig. 1 (a) Schematic representation of the distribution of cations C and anions A between the solution and the membrane having fixed ionic groups G; (b) Donnan relation and electroneutrality conditions in the solution and membrane. c and $\bar{c}$ are the molar ion concentration at equilibrium in the solution and membrane, respectively. v_+ and v_- are the stoichiometric coefficients

of cations and anions, respectively. z_C and z_A are the charge numbers of cations and anions, respectively. The symbol X (positive or negative depending on the charge sign of the membrane) denotes the volume charge density, which is defined as the number of moles of fixed charges per unit of pore volume

To illustrate the influence of various parameters on the Donnan equilibrium, let us consider the equilibrium situation between a membrane containing fixed ionic groups G and an ionic solution containing the strong electrolyte CA (Fig. 1).

Based on the Donnan equilibrium and taking the electroneutrality conditions into account, the partitioning coefficient of co-ions at the membrane-solution interface ($k_{\text{co-ion}}$), which describes the distribution of co-ions between the membrane and the solution, can be derived:

$$k_{\text{co-ion}} = \frac{\bar{c}_{\text{co-ion}}}{c_{\text{co-ion}}} = \left(\frac{z_{\text{co-ion}} c_{\text{co-ion}}}{z_{\text{co-ion}} \bar{c}_{\text{co-ion}} + X} \right) \left(\left| \frac{z_{\text{co-ion}}}{z_{\text{counterion}}} \right| \right) \quad (1)$$

with $c_{\text{co-ion}}$ and $\bar{c}_{\text{co-ion}}$ the concentrations of co-ions in the solution and membrane, respectively, and $z_{\text{co-ion}}$ and $z_{\text{counterion}}$ the charge numbers of co-ions and counterions, respectively.

A co-ion partitioning coefficient that tends to one means that co-ions (and therefore counterions due to electroneutrality requirements) are only slightly excluded from the membrane (weakly charged membrane, small $|X|$), whereas a co-ion partitioning coefficient that tends to zero means that the co-ions are strongly excluded from the membrane (strongly charged membrane, high $|X|$).

Donnan Effect, Table 1 Calculation of the co-ion partitioning coefficient ($k_{\text{co-ion}}$) at a membrane-solution interface for a (positively or negatively charged) membrane with a fixed charge $|X|$ of $10^{-2} \text{ mol L}^{-1}$ and various salts and concentrations

$c_{\text{co-ion}} (\text{mol L}^{-1})$	$ z_{\text{co-ion}} $	$ z_{\text{counterion}} $	$k_{\text{co-ion}}$
10^{-4}	1	1	0.01
10^{-3}	1	1	0.10
10^{-2}	1	1	0.62
10^{-3}	1	2	0.31
10^{-3}	2	1	0.04

Solving Eq. 1 allows the concentration of co-ions in the membrane ($\bar{c}_{\text{co-ion}}$) and, thus, the partitioning coefficient of co-ions ($k_{\text{co-ion}}$) to be calculated. Results presented in Table 1 show that exclusion increases ($k_{\text{co-ion}}$ decreases) when:

- The salt concentration (or $c_{\text{co-ion}}$) decreases
- The charge number of co-ions $z_{\text{co-ion}}$ increases
- The charge number of counterions $z_{\text{counterion}}$ decreases
- The fixed membrane charge (in absolute value) X increases.

The increase (in absolute value) in the fixed charge and electrolyte concentration has then opposite effects on the exclusion phenomenon since the former makes the Donnan effect stronger, whereas the latter screens the electrostatic interaction between ions and the membrane fixed

Donnan Effect, Table 2 Calculation of the co-ion partitioning coefficient ($k_{\text{co-ion}}$) at a membrane-solution interface for various membrane volume charges $|X|$, salts, and concentrations

Salts	c_{salt} (mol L^{-1})	$Z_+ V_+$ $c_{\text{salt}} = Z_- V_-$ c_{salt}	$ X $ (mol L^{-1})	$\frac{ X }{Z_+ V_+ c_{\text{salt}}}$	$k_{\text{co-ion}}$
1:1	10^{-3}	10^{-3}	10^{-2}	10	0.10
1:1	10^{-2}	10^{-2}	10^{-1}	10	0.10
1:2	5×10^{-4}	10^{-3}	10^{-2}	10	0.01
1:2	5×10^{-3}	10^{-2}	10^{-1}	10	0.01
2:1	5×10^{-4}	10^{-3}	10^{-2}	10	0.31
2:1	5×10^{-3}	10^{-2}	10^{-1}	10	0.31
2:2	5×10^{-4}	10^{-3}	10^{-2}	10	0.10
2:2	5×10^{-3}	10^{-2}	10^{-1}	10	0.10

Salt 1:2: salt with a monovalent counterion and divalent co-ion
Salt 2:1: salt with a divalent counterion and monovalent co-ion
Salt 1:1: salt with a monovalent counterion and monovalent co-ion
Salt 2:2: salt with a divalent counterion and divalent co-ion

charge. As a result, as can be seen in Table 2, the co-ion partitioning coefficient is ruled by the ratio of the membrane fixed charge (in absolute value) to the charge concentration in solution, $\frac{|X|}{Z_+ V_+ c_{\text{salt}}}$. Table 2 also shows that for salt solutions having the same charge concentration, the co-ion partitioning coefficients are identical for salts 1:1 and 2:2, and $k_{\text{co-ion}}$ follows the sequence $2:1 > 1:1 = 2:2 > 1:2$ where the first figure denotes the charge number of the counterion and the second one that of the co-ion.

The increase of co-ion exclusion from the membrane leads to a higher salt rejection since the latter is determined by rejection of co-ions.

Cross-References

- [Donnan Equilibrium](#)
- [Donnan Potential](#)

References

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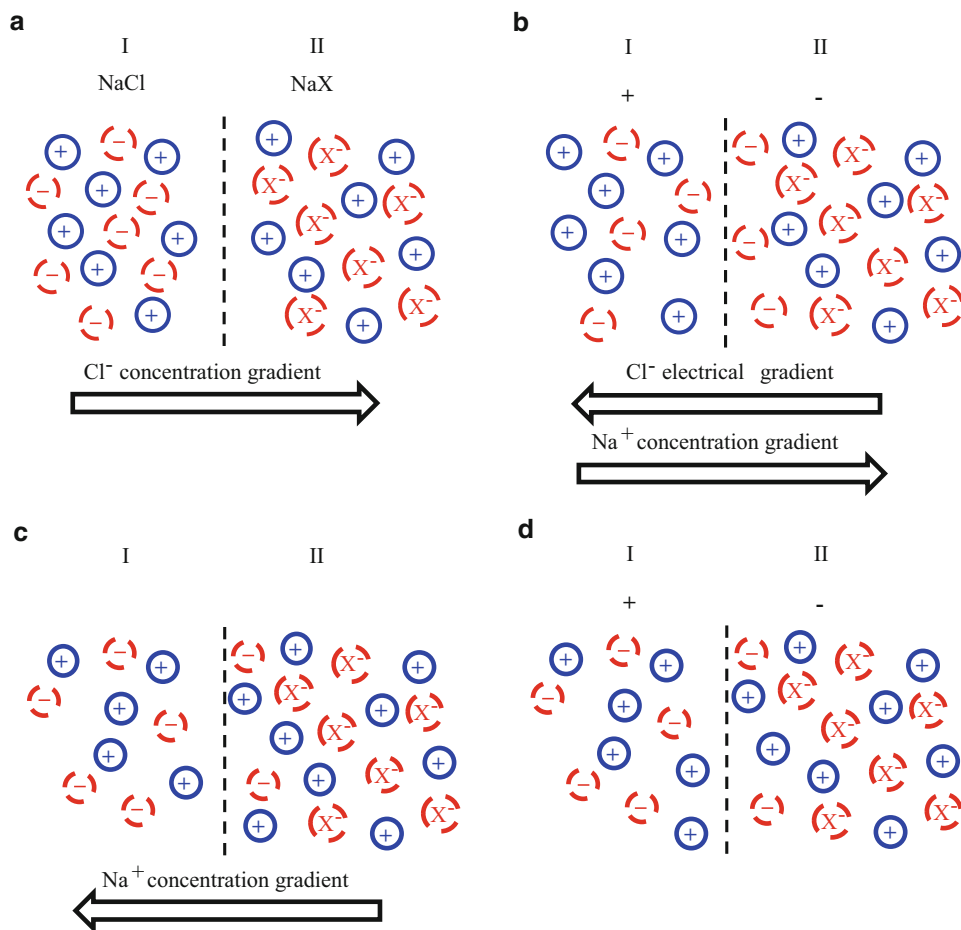
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Donnan Equilibrium

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The Donnan equilibrium describes the distribution of ions between two ionic solutions separated by a semipermeable membrane or boundary. The presence of impermeant ions of one side of the boundary has profound effects on the final distribution of permeant ions as they diffuse to an equilibrium in the solution, which is named after the British chemist Frederick George Donnan (1911, 1995).

To illustrate this phenomenon, let us consider a boundary that initially separates a solution of NaCl (side I) and a solution of NaX (side II), NaCl and NaX being completely dissociated and having the same molar concentrations, and let us assume that the boundary is impermeable to the anion X^- , but completely permeable to both Na^+ and Cl^- ions (Fig. 1a). X^- can be, e.g., an anionic protein inside a cell, the walls of which are impermeable to the protein or surface charged groups (such as, e.g., sulfonic or carboxylic acids) of a synthetic membrane. Since side II does not contain Cl^- ions, Cl^- ions diffuse along the concentration gradient from side I to side II (Fig. 1a). The presence of both Cl^- anions plus impermeable anions on side II makes side II negative relative to side I and establishes an electric potential



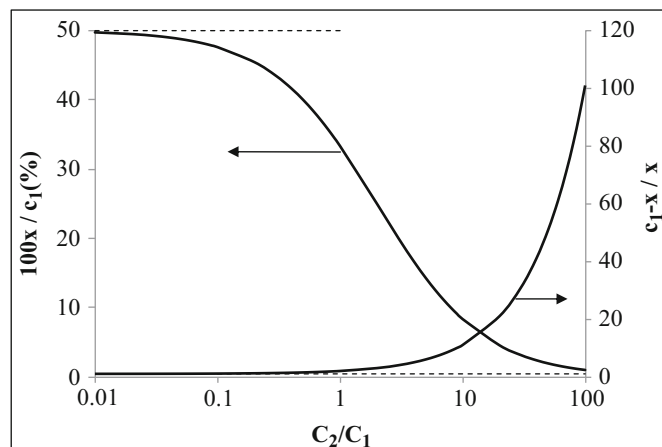
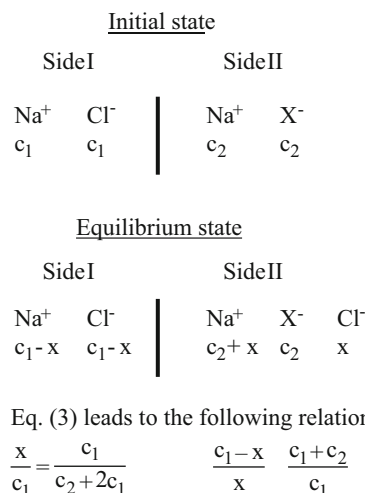
Donnan Equilibrium, Fig. 1 Illustration of the establishment of Donnan equilibrium between two solutions (NaCl and NaX) separated by a boundary permeable to K^+ and Cl^- ions but impermeable to the anion X^-

difference at the boundary between sides I and II (Fig. 1b). The development of the negative charge on side II counterbalances the concentration gradient of Cl^- ions and prevents Cl^- concentration from becoming equal on both sides of the membrane. At the same time, the negative charge on side II attracts the positive Na^+ ions to migrate from side I to side II along the electrical gradient. The Na^+ concentration on side II now exceeds that of side I, and Na^+ ions will diffuse back from side II to side I along the concentration gradient (Fig. 1c). At equilibrium, the competing electrical potential and concentration gradients for each ion are in balance and there is no net flow of ions through the membrane (Fig. 1d). Na^+ and Cl^- ions move back and forth between sides I and II in

response to the competing electrochemical gradient so that each side remains electrically neutral due to equal molar concentrations of both cations and anions. Between the two sides, there is unequal distribution of permeant ions with the more total anions on side II. This imbalance in the distribution of permeant ions results in an electrical potential difference between sides I and II, which is called the Donnan potential.

At equilibrium, the electrochemical potentials of the ions on side I and side II are equal, hence:

$$\begin{aligned} \mu_i^{0,I} + RT \ln a_i^I + z_i F \psi^I \\ = \mu_i^{0,II} + RT \ln a_i^{II} + z_i F \psi^{II} \end{aligned} \quad (1)$$



Donnan Equilibrium, Fig. 2 Effect of the initial concentration ratio of NaX (c_2) to NaCl (c_1) on the percentage amount of NaCl diffusing from side I to side II ($100 x/c_1$)

and the distribution ratio of NaCl between sides I and II at equilibrium ($c_1 - x/x$)

where μ_i^0 represents the standard chemical potential of the permeant ion i , a_i is its activity, z_i is its charge number, Ψ is the electric potential, R is the ideal gas constant, T is the temperature, and F is the Faraday constant. The superscripts I and II refer to the side I and side II, respectively.

In the derivation of the electrochemical potential, the difference in pressure between sides I and II is neglected. In the case of a synthetic membrane, this assumption can be justified if its swelling is negligible.

Assuming that the standard chemical potentials on sides I and II are equal, the Donnan potential (defined as the potential difference between the side of the boundary with the impermeant ion and the side with the permeant ions) can be calculated for each permeant ion i as:

$$\Delta\psi_D = \psi^{II} - \psi^I = \frac{RT}{z_i F} \ln \frac{a_i^I}{a_i^{II}} \quad (2)$$

The writing of Eq. 2 for permeant ions Na⁺ and Cl⁻ (assuming sufficiently diluted solutions) and the combination of the two resulting equations lead to the so-called Donnan (or Gibbs-Donnan) equation:

$$[\text{Na}^+]_1 [\text{Cl}^-]_1 = [\text{Na}^+]_2 [\text{Cl}^-]_2 \quad (3)$$

where the square brackets indicate molar concentrations at equilibrium.

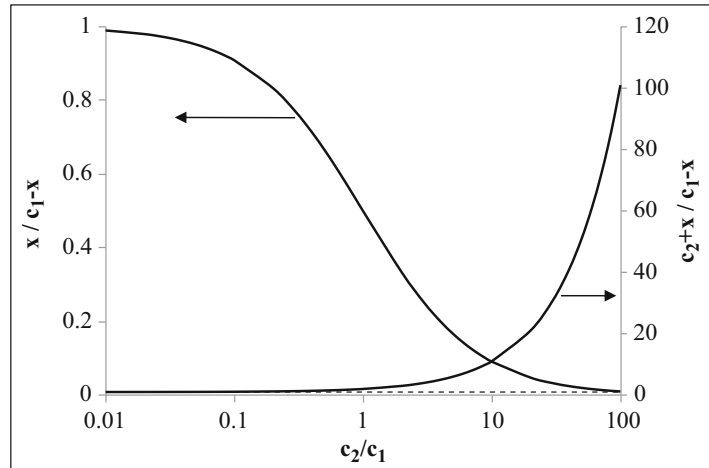
It should be noted that Donnan equation Eq. 3 was derived without considering the initial concentrations of NaCl and NaX on sides I and II, respectively.

Figure 2 shows the effect of the initial concentration ratio of NaX (c_2) to NaCl (c_1) on the percentage amount of NaCl diffusing from side I to side II ($100 x/c_1$) and the distribution ratio of NaCl between sides I and II at equilibrium ($c_1 - x/x$). These results are obtained by making the assumption that the liquid volumes on both sides of the membrane are equal.

As can be seen, if the relative concentration of NaX on side II is high enough ($c_2 \gg c_1$), NaCl will be expelled to a large extent from side II to side I and the distribution of NaCl between I and II will be then very unequal, whereas, on the other hand, more NaCl (up to 50 %) will be able to flow from side I to side II with decreasing c_2/c_1 and the distribution ratio of NaCl between I and II will tend then to 1. At equilibrium, the concentration of Cl⁻ ions (i.e., ions with the same charge polarity as the impermeant ions) on side II will be lower than that on side I, whereas the Na⁺ ions (i.e., ions having the charge polarity opposite to that of the

Donnan Equilibrium,

Fig. 3 Effect of the initial concentration ratio of NaX (c_2) to NaCl (c_1) on the concentration ratio of both Cl^- ions ($x/c_1 - x$) and Na^+ ions ($c_2 + x/c_1 - x$) between sides II and I at equilibrium



impermeant ions) will have a higher concentration on side II than on side I (Fig. 3).

Cross-References

► [Donnan Potential](#)

References

- Donnan FG (1911) Theorie der Membrangleichgewichte und Membranpotentiale bei Vorhandensein von nicht dialysierenden Elektrolyten. Ein Beitrag zur physikalisch-chemischen Physiologie (theory of membrane equilibria and membrane potentials in the presence of non-dialyzing electrolytes. A contribution to physical-chemical physiology). *Z Elektrochem Angew Phys Chem* 17(10):572–581
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Donnan Potential

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The Donnan potential appears as a result of Donnan equilibrium, which refers to the distribution of ions between two ionic solutions separated

by a semipermeable membrane or boundary. Because of the presence of impermeant ion species on one side of the boundary, the concentrations of permeant ions are not the same on both sides of the boundary. These concentration differences between two solutions lead to chemical potential differences across the boundary and these differences will, on their turn, be compensated by an additional electric potential difference between two solutions. At equilibrium, the electrochemical potentials of permeant ions in two solutions are identical. Assuming their standard chemical potentials are equal, the electric potential difference between two solutions, which is called the Donnan potential ($\Delta\Psi_D$), can then be derived:

$$\Delta\Psi_D = \Psi^{\text{II}} - \Psi^{\text{I}} = \frac{RT}{z_i F} \ln \frac{a_i^{\text{I}}}{a_i^{\text{II}}} \quad (1)$$

with ψ the electric potential, R the ideal gas constant, T the absolute temperature, F the Faraday constant, z_i the charge number of ion i , and a_i its activity. The superscript I and II refer to the solution without impermeant ions and the solution with impermeant ions, respectively.

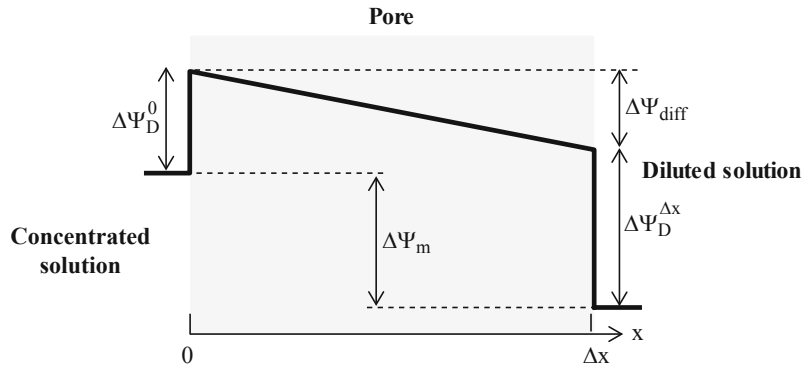
The impermeant ions may be, e.g., anionic proteins inside a cell whose walls are impermeable or fixed charges of a synthetic membrane.

Equation 1 shows that:

- The Donnan potential will be negative in case of anionic impermeant species (membrane

Donnan Potential,

Fig. 1 Schematic representation of the electric potential distribution in a pore under a concentration difference. $\Delta\psi_D^0$ and $\Delta\psi_D^{\Delta x}$: Donnan potentials at interfaces. $\Delta\psi_{diff}$: diffusion potential. $\Delta\psi_m$: membrane potential



with a negative fixed charge) and positive in case of impermeant cations (membrane with a positive fixed charge).

- The co-ions, i.e., ions with the same charge polarity as the impermeant ions (the latter can be the fixed charges of a synthetic membrane), will be less concentrated on the impermeant ions' side than the other side, whereas the counterions, i.e., ions having the charge polarity opposite to that of the impermeant ions, will be more concentrated there. It results in an unequal distribution of permeant ions (co-ions and counterions) between the two sides.

The Donnan potential is used in the Teorell-Meyer-Sievers (TMS) model (Teorell 1935; Meyer and Sievers 1936) and related models such as the DSP&DE model (Lanteri et al. 2008; Escoda et al. 2010), which notably describe the membrane potential phenomenon. The membrane potential is defined as the electrical potential difference arising through a membrane that separates two solutions of the same electrolyte at the same temperature and hydrostatic pressure but different concentrations. Within the scope of the TMS model (and related models), the membrane potential ($\Delta\psi_m$) is split in two components, namely, the difference between the Donnan potentials at each interface ($\Delta\psi_D^{\Delta x}$ and $\Delta\psi_D^0$: superscripts Δx and 0 refer to the interface between the membrane and the most diluted solution and the interface between the membrane and the most concentrated solution, respectively) and the diffusion potential

($\Delta\psi_{diff}$) arising through the membrane pores (Fig. 1):

$$\Delta\psi_m = \Delta\psi_D^{\Delta x} - \Delta\psi_D^0 + \Delta\psi_{diff} \quad (1)$$

The diffusion potential finds its origin in a difference in transport velocity of cations and anions through the membrane.

Within the scope of the DSP&DE model, ion partitioning at the membrane/solution interfaces is accounted for by means of modified Donnan equations including steric and dielectric effects. The Donnan potential reads as follows:

$$\Delta\psi_D^{int} = \bar{\psi}^{int} - \psi^{int} = \frac{k_B T}{z_i e} \ln \left(\frac{\kappa_i^{int} c_i^{int}}{\bar{c}_i^{int}} \right) \quad (2)$$

with

$$\kappa_i^{int} = \phi_i^{int} \exp(-\Delta W_{i,Born}^{int}) \exp(-\Delta W_{i,image}^{int}) \quad (3)$$

k_B is the Boltzmann constant; T is the absolute temperature; e is the elementary charge; z_i is the charge number of ion i ; ϕ_i^{int} represents the steric partitioning coefficient for ion i , which is defined as the ratio between the available section (i.e., taking into account the zone inside the pore in which the ion center cannot penetrate because of its finite size) and the pore cross-section; and the terms $\Delta W_{i,Born}^{int}$ and $\Delta W_{i,image}^{int}$ denote the increase in the interaction energy due to the Born dielectric effect (Born 1920) and image forces (Dukhin

et al. 1988), respectively, where the prime symbol indicates that both terms are scaled on $k_B T$.

According to Eq. 2, the difference in Donnan potentials, called the Donnan term, is given by (considering $c_i^0 = 2c_i^{\Delta x}$):

$$\Delta\Psi_D^{\Delta x} - \Delta\Psi_D^0 = \frac{k_B T}{z_i e} \ln \left(\frac{\kappa_i^{\Delta x} \bar{c}_i^0}{2\kappa_i^0 \bar{c}_i^{\Delta x}} \right) \quad (4)$$

- For charged membranes, the membrane potential is bound between limiting values corresponding to the Nernst potential at low concentrations and the diffusion potential at high concentrations (Lanteri et al. 2008; Escoda et al. 2010). The Nernst potential corresponds to the asymptotic value of the Donnan term when the co-ion exclusion is total. If the membrane volume charge density is assumed to be independent of the axial position inside pores, the concentration of counterions inside pores is then constant too ($\bar{c}_{\text{counterion}}^0 = \bar{c}_{\text{counterion}}^{\Delta x}$) and Eq. 4 can be rewritten as:

$$\Delta\Psi_D^{\Delta x} - \Delta\Psi_D^0 = \frac{k_B T}{z_{\text{counterion}} e} \ln \left(\frac{\kappa_{\text{counterion}}^{\Delta x}}{2\kappa_{\text{counterion}}^0} \right) \quad (5)$$

Moreover, the steric partitioning coefficients are identical at both interfaces ($\phi_i^0 = \phi_i^{\Delta x} \neq 0$) since the pore radius is assumed to be constant through the membrane. Born effect is also identical at both interfaces ($\Delta W_{i,\text{Born}}^0 = \Delta W_{i,\text{Born}}^{\Delta x} \neq 0$), since it is considered to be independent of the salt concentration. Unlike Born effect, the magnitude of the interaction via image charges depends on concentration. However, there is almost no screening of the image force interaction at low concentrations, and thus, $\Delta W_{i,\text{image}}^0 = \Delta W_{i,\text{image}}^{\Delta x} \neq 0$. It results that $\kappa_{\text{counterion}}^0 = \kappa_{\text{counterion}}^{\Delta x}$. Equation 5 then reduces to:

$$\Delta\Psi_D^{\Delta x} - \Delta\Psi_D^0 = \frac{k_B T}{z_{\text{counterion}} e} \ln(2) \quad (6)$$

which represents the Nernst potential (the value of which is inversely proportional to the charge number of counterions).

In high concentrations, the Donnan contribution tends to zero (the asymptotic value of the membrane potential is then equal to the diffusion potential) due to the screening of both membrane fixed charge density and image force interaction ($\Delta W_{i,\text{Born}}^0 \approx \Delta W_{i,\text{Born}}^{\Delta x} \approx 0$).

- For neutral membranes and when the only exclusion mechanism is the steric exclusion (i.e., $\kappa_i^{\text{int}} = \phi_i^{\text{int}}$) or the Born dielectric exclusion ($\kappa_i^{\text{int}} = \exp(-\Delta W_{i,\text{Born}}^{\text{int}})$) or both ($\kappa_i^{\text{int}} = \phi_i^{\text{int}}, \exp(-\Delta W_{i,\text{Born}}^{\text{int}})$), the Donnan contribution is null irrespective of the concentration. It means that Donnan potentials are equal at both interfaces although each of them differs from zero. Indeed, since cations and anions have usually different sizes, their steric partitioning coefficients are different as well as their terms $\Delta W_{i,\text{Born}}^{\text{int}}$. The smallest ions (e.g., the anions) will be then less excluded than the largest ones (e.g., the cations). Consequently, a slight negative Donnan potential will arise, pulling cation ions into pores and expelling anions to maintain electroneutrality within the membrane. Since only steric effects or only Born dielectric effect or both are considered, one obtains $\kappa_i^0 = \kappa_i^{\Delta x}$. Considering the electroneutrality condition within the membrane, it comes from Eq. 4 that the Donnan potentials are identical at both interfaces, and thus the Donnan contribution to the membrane potential arising through a neutral membrane is null whatever the concentration.

Cross-References

- [Donnan Equilibrium](#)
- [DSP&DE Model Applications](#)

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Donnan Steric Pore (DSP) and Dielectric Exclusion (DE) Model

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The Donnan steric pore (DSP) and dielectric exclusion (DE) model (known as the SEDE model in literature) is a model that describes mass transfer of neutral and charged solutes through *nanofiltration* (NF) membranes (Szymczyk and Fievet 2005). It is based on a macroscopic description of transport and is an extension of the Donnan steric pore model (DSPM) firstly proposed by Bowen and Mukhtar (1996) and then revised in Bowen et al. (1997) and in Bowen and Mohammad (1998). In addition to the steric/electric exclusion mechanisms, the DSP and DE model also includes

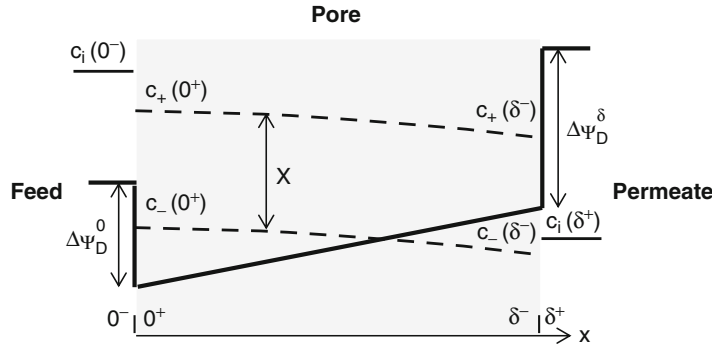
dielectric effects. Its main features can be summarized as follows:

- The active layer of the membrane is considered as a charged porous layer and is characterized by means of three adjustable parameters: the average pore radius r_p , the effective membrane thickness δ (including tortuosity or porosity and tortuosity of the active layer depending on the model version), and the volume charge density X (defined as the mole number of fixed charges per unit of pore volume), which is assumed to be constant along the membrane pores. The presence of the coarse-porous support layer is disregarded because it does not affect the retention properties of the membrane.
- The radial variations of both local electric potential and ion concentrations inside the nanopores are neglected. This approximation (called homogeneous approximation) is valid provided the electric charge carried out by the nanopore walls is not too high (Szymczyk et al. 1999).
- Membrane separation is described as being the result of the following steps: first, a distribution of species at the membrane/feed solution interface, followed by solute transport through the pores, and finally a distribution of species at the membrane/permeate interface (Fig. 1).
- The solute transport is based on the extended Nernst–Planck (ENP) equation, which describes transport in terms of diffusion, migration (in the case of ions only), and convection. It is modified by hydrodynamic coefficients ($K_{i,c}$ and $K_{i,d}$) accounting for the effect of finite pore size on the various components of the transport and reads as follows:

$$j_i = -K_{i,d}D_{i,\infty} \frac{d\bar{c}_i}{dx} - \frac{z_i\bar{c}_iK_{i,d}D_{i,\infty}F}{RT} \frac{d\psi}{dx} + K_{i,c}\bar{c}_iV \quad (1)$$

Note for editors: The model developed by Bandini and Vezzani is known as the DSP and DE model. However, their model considers dielectric exclusion in terms of the only image force contribution. My suggestion, therefore, would be to replace the topic title “Donnan Steric Pore (DSP) and Dielectric Exclusion (DE) Model” by the title “SEDE (Steric, Electric, and Dielectric Exclusion) Model,” which includes dielectric exclusion in terms of both Born dielectric effect and image force contribution. It would avoid confusion. Indeed, I wrote this topic by considering my model, namely, the SEDE model, which was developed by Szymczyk and me. However, as requested by the editors, I did use the term DSP and DE in the text below.

- where j_i is the molar flux of specie i through the pores; $D_{i,\infty}$ its diffusivity in the external solution (value at infinite dilution); $\bar{c}_i$ its



Donnan Steric Pore (DSP) and Dielectric Exclusion (DE) Model, Fig. 1 Schematic representation of a pore separating a feed solution (*high-pressure side*) from a permeate (*low-pressure side*) and concentration and

electric potential profiles. Mono-monovalent salt and negatively charged membrane ($X < 0$). $\Delta\psi_D^{\text{int}}$: Donnan potential (superscript int stands for 0 or δ)

concentration inside the pores at the x position along the pore; z_i its charge number; ψ and V are the local electric potential and the solvent velocity inside the pores, respectively; R the ideal gas constant; T the absolute temperature; and F the Faraday constant.

Hydrodynamic coefficients $K_{i,c}$ and $K_{i,d}$ depend on the solute to pore size ratio, λ_i , defined as $\lambda_i = r_{i,\text{Stokes}}/r_p$ where $r_{i,\text{Stokes}}$ is the Stokes radius of the solute which is calculated using the well-known Stokes–Einstein relation:

$$r_{i,\text{Stokes}} = \frac{k_B T}{6\pi\eta D_{i,\infty}} \quad (2)$$

with k_B the Boltzmann constant and η the solvent viscosity.

The meaning and relevance of hindrance factors ($K_{i,c}$ and $K_{i,d}$) have been widely documented by Deen (Deen 1987) as well as by many other authors (Mason et al. 1980; Deen et al. 1980; Nakao and Kimura 1982; Bowen and Sharif 1994).

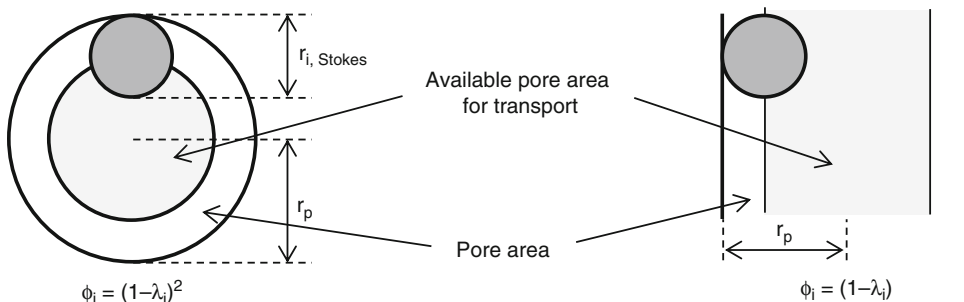
- The partition coefficient of a solute i at the membrane/external solution interfaces (defined as $\bar{c}_i^{\text{int}}/c_i^{\text{int}}$), which is derived by assuming local thermodynamic equilibrium, is given by:

$$\begin{aligned} \Gamma_i^{\text{int}} &= \frac{\bar{c}_i^{\text{int}}}{c_i^{\text{int}}} \\ &= \Phi_i^{\text{int}} \exp\left(-\frac{z_i e}{k_B T} \Delta\psi_D^{\text{int}}\right) \\ &\quad \exp\left(-\Delta W_{i,\text{Born}}^{\text{int}}\right) \exp\left(-\Delta W_{i,\text{image}}^{\text{int}}\right) \end{aligned} \quad (3)$$

where the superscript int stands for 0 or δ depending on the interface that is considered, the symbol Δ denotes a variation with respect to external solutions, and e is the elementary charge.

The first term on the r.h.s. represents the contribution of the steric exclusion, Φ_i being the steric partitioning coefficient for solute i , which is defined as the ratio between the available section (i.e., taking into account the zone inside the pore in which the ion center cannot penetrate because of its finite size) and the pore cross section (Fig. 2). The steric partitioning coefficient is bounded between 0 and 1, $\Phi_i^{\text{int}} = 1$ for point solutes, whereas $\Phi_i^{\text{int}} = 0$ for solutes larger than the pore. It should be noted that for a neutral solute, the partition coefficient is written as: $\Gamma_i^{\text{int}} = \Phi_i^{\text{int}}$ (due to its zero charge).

$\Delta\psi_D^{\text{int}}$ is the *Donnan potential* involved in the electric exclusion mechanism (Fig. 1). By definition, it has the same sign as the membrane charge. As shown by the second term on the r.h.s. of Eq. 3, the *Donnan potential* is repulsive for co-ions



Donnan Steric Pore (DSP) and Dielectric Exclusion (DE) Model, Fig. 2 Schematic representation of available pore area for transport in a cylindrical (a) and slit-like (b) pore. Φ_i : steric partitioning coefficient; $\lambda_i = r_{i, \text{Stokes}}/r_p$

(i.e., ions having the same charge polarity as the membrane) and attractive for counterions (i.e., ions with the charge polarity opposite to that of the membrane).

Finally, the terms $\Delta W_{i, \text{Born}}^{\text{int}}$ and $\Delta W_{i, \text{image}}^{\text{int}}$ denote the increase in the interaction energy (scaled on $k_B T$) of ion i due to the Born and image force dielectric effects, respectively.

The Born dielectric effect is connected with the lowering of the dielectric constant of the solution inside pores ϵ_p (with respect to the corresponding value in the external bulk solution ϵ_b) caused by an alteration of the solvent structure when it is confined in nanodimensional pores. The variation of the interaction energy resulting from the Born effect is given by:

$$\Delta W_{i, \text{Born}}^{\text{int}} = \frac{(z_i e)^2}{8\pi\epsilon_0 k_B T r_{i, \text{cav}}} \left(\frac{1}{\epsilon_p} - \frac{1}{\epsilon_b} \right) \quad (4)$$

where ϵ_0 is the vacuum permittivity and $r_{i, \text{cav}}$ is the cavity radius of ion i .

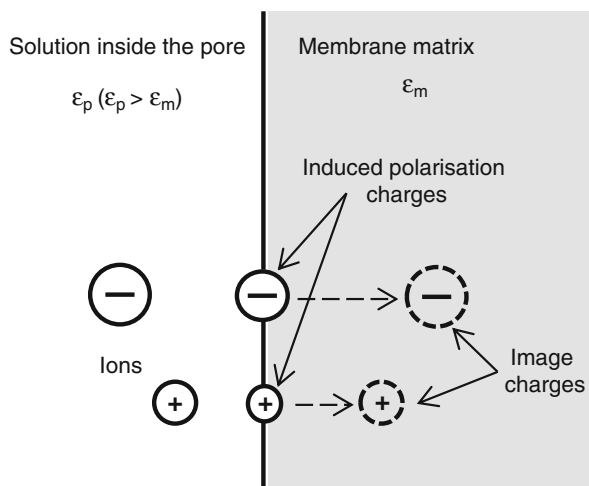
Equation 4 is similar to the relation derived in the original Born model (Born 1920) for ion-solvent interactions except that the radius of the cavity formed by the ion i in the solvent ($r_{i, \text{cav}}$) is used here (Rashin and Honig 1985; Hyun and Ichiye 1997; Qiu et al. 1997) instead of the ionic radius as stated in the original Born model (which is known to overestimate solvation enthalpies, especially for cations).

As shown by Eq. 4, the partition due to the Born DE is unfavorable for any ion, independently of the ion polarity (provided $\epsilon_p < \epsilon_b$), and

multivalent ions are more strongly rejected than monovalent ones. Moreover, the Born effect does not depend on pore size and geometry.

The interaction free energy of an ion inside a pore of nanometric dimensions is also affected by the interaction of the ion with the polarization charge induced by the ion itself at the interface between the membrane matrix and the solution inside the pore (Parsegian 1969; Dresner 1974; Glueckauf 1976). This phenomenon results from the difference in dielectric constants between the membrane and the solution and is usually described as the production of image forces (Dukhin et al. 1988) since the interaction between the ion and the polarized interface is formally equivalent to the interaction with a fictitious image charge located at the other side of the interface at the same distance from it as the ion (Fig. 3). This topic has been reviewed recently by Yaroshchuk (2000) who derived approximate expressions for the interaction energy in pores of cylindrical and slit-like geometries. These equations, which are complex, account for the screening of the interaction between the ion and the polarized interface by the membrane fixed charge and the ionic atmosphere as well.

Like the Born effect, this dielectric effect is also controlled by the square of the ion charge. Consequently, it does not differentiate (qualitatively) between co-ions and counterions (unlike the Donnan exclusion which repels co-ions but attracts counterions), and both co-ions and counterions are excluded from the membrane pores provided $\epsilon_m < \epsilon_p$.



Donnan Steric Pore (DSP) and Dielectric Exclusion (DE) Model, Fig. 3 Schematic representation of the interaction of ions with their polarization charge induced by the ions themselves at the interface between the solution inside the pore and the membrane matrix. Image charges can be used to visualize the force arising from the dielectric

discontinuities. It should be noted that the physical effect is the induced polarization charges at the interface whereas the image charge is just a tool to construct an equivalent system where the net interaction is the same (Jonssön and Wennerström 1983)

Last, it should be noted that DE (Born and image forces) plays a relevant role even in the case of uncharged membranes for which Donnan exclusion is zero.

Cross-References

- [Donnan Potential](#)
- [Nanofiltration](#)

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Dope Solution

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Dope solution is a homogeneous thermodynamically stable polymer solution formed by a polymer or a copolymer, solvent or a solvent mixture, and/or additive(s) (i.e., the additive can be a second polymer, a non-solvent, organic or inorganic particles of different sizes, etc.). It is also possible to add a non-solvent to the polymer solution to such an extent that all the components are still miscible. In this case, care must be taken because demixing may occur by the addition of the non-solvent to the polymer solution so that it becomes thermodynamically unstable. Sometimes nanoparticles or nanotubes are dispersed in the polymer solution.

To prepare a dope solution, the polymer must be soluble in a solvent or a solvent mixture. The solvent has a close solubility parameter with the polymer. The solvent and the non-solvent must be miscible and the viscosity of the dope solution must be high (i.e., more than 100 P).

After preparing the polymer solution, this should be filtered to remove impurities and insoluble contaminants. Subsequently, the resulted dope solution should be degassed before loading into the dope vessel for fabrication of either flat sheet or ► [hollow fiber](#) membranes. The spinning dope suitable for ► [hollow fiber](#) fabrication by dry/wet spinning or wet spinning techniques

generally has a much greater viscosity and elasticity than that used for the fabrication of flat sheet membranes by the phase inversion technique.

The used polymer limits the solvent(s) and the non-solvent(s) that can be used to prepare the dope solution for the phase inversion process. Water is frequently used as a non-solvent. For example, among others, the solvents dimethyl formamide (DMF) and dimethyl acetamide (DMAC) were used to prepare dope solutions from polysulfone, poly(ether sulfone), poly(vinylidene fluoride), polyacrylonitrile, cellulose acetate, polyimide, or poly(ether imide).

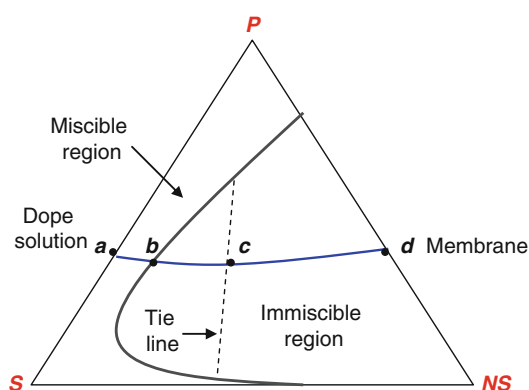
To prepare membranes by thermal precipitation, for example, thermally induced phase inversion (TIPS) membranes, the dope solution is a polymer/diluent system adequate to form a homogeneous melt blend, which will be cooled or quenched to induce phase separation (i.e., liquid–liquid phase separation, solid–liquid phase separation, or combined liquid–liquid and solid–liquid phase separation). For TIPS mechanism the diluent should be miscible with the considered polymer at high temperatures, should have a relatively low molecular weight together with a low volatility at high temperatures, and should be thermally stable at high temperatures. For example, the used diluent for poly(vinylidene fluoride), PVDF, is dimethyl phthalate, dioctyl phthalate, dioctyl sebacate, dibutyl phthalate, γ -butyrolactone, propylene carbonate, or dibutyl sebacate.

The parameters affecting the physical and chemical characteristics of the dope solution are the polymer, the solvent(s), the non-solvent additive(s), and their concentrations as well as the temperature. These characteristics affect the structural morphology of the formed flat sheet membranes and hollow fibers. The polymer concentration in the dope solution is one of the relevant factors affecting membrane structure. For example, the increase of the polymer concentration in the dope solution results in a high-volume fraction of polymer and consequently a low porosity and small pore size. A significant reduction of the porosity was observed with increasing PVDF concentration in the spinning dope from 15 to

20 wt% (Wu et al. 2007). However, over this PVDF concentration range, no apparent effect on the mean pore size of the prepared hollow fibers was observed. Fabrication of membranes by the phase inversion technique from dope solutions with a very low polymer concentration is practically impossible. For instance, when the polymer content is less than a threshold value, for example, 10 wt% for PVDF, the resulting membranes become inconsistent and holes start to appear within the membrane (Ortiz de Zárate et al. 1995). In the phase inversion process, non-solvent additive in the dope solution acts as a pore-forming agent improving the permeability of the fabricated phase inversion membrane. In general, when the concentration of the non-solvent additive is increased in the dope solution, the pore size and porosity of the prepared membrane increase (Khayet and Matsuura 2001).

The maximum amount of non-solvent that can be added to a dope solution can be determined from the ternary phase diagram presenting the composition of the polymer, solvent, and the non-solvent. In this case, the dope solution must be in one phase region where all the components are completely miscible with each other. Figure 1 shows an isothermal ternary system (polymer, P ; solvent, S , non-solvent, NS). The pure components (P , S , NS) are localized at the corners of the triangle, and any point within the triangle represents a mixture of all three components. Within a certain compositionally defined range of thermodynamic states, all three components are completely miscible, whereas in a different range, the system decomposes into two distinct phases. The solid black line is the liquid-liquid boundary, called the binodal which separates the miscible region at the left from the immiscible region at the right. The thermodynamic parameter describing the miscibility of two or more components (e.g., polymer and diluent) is the Gibbs free energy of mixing, for which an expression was given by the Flory-Huggins lattice theory (Flory 1965).

During membrane preparation, the dope solution at the left side of the binodal in the P - S axis is immersed in a non-solvent so that the final



Dope Solution, Fig. 1 Schematic phase diagram of an isothermal ternary system (polymer, P ; solvent, S and non-solvent, NS)

composition will be displaced to the right side in the phase diagram toward the P - NS axis. Different composition paths can occur (Khayet and Matsuura 2011). For example, the path (a , b , c , d) starts from a dope solution with a low initial polymer volume fraction on the P - S axis and the ratio of the rate of solvent outflux to that of the non-solvent influx is relatively high. When the dope solution crosses the binodal, two separate phases will begin to form. Those are a polymer-rich phase represented by the upper end of the tie line and a polymer-poor phase represented by the lower end of the tie line. If the amount of the polymer-rich phase is large relative to the amount of the polymer-poor phase, droplets of the latter phase are dispersed in the continuous polymer-rich phase and form pores in the continuous polymer matrix. The obtained final membrane at the P - NS axis is asymmetric (i.e., a dense surface layer at the film/gelation media interface followed by a porous sub-layer). The film composition starts from the point " a ," passes through points " b " and " c " (polymer densification point), and finally reaches the point " d " along the composition path. " b " is the point where the phase separation starts and " c " is the point where the polymer solidification starts to occur. Exchange of solvent and non-solvent will lead to the final formation of the membrane, the porosity of which is determined by the point on the P - NS line (e.g., point " d ") (Khayet and Matsuura 2011).

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Double Emulsion

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Synonyms

Multiple emulsions

Double emulsion is a complex system of an emulsion in an emulsion, where the droplets of the dispersed phase themselves contain even smaller dispersed droplets. An [emulsion](#) is a dispersion of droplets of one liquid in another one with which it is incompletely miscible.

Two main types of double emulsion can be distinguished: water-in-oil-in-water (W/O/W) emulsion, in which a W/O emulsion is dispersed as droplets in an aqueous phase, and oil-in-water-in-oil (O/W/O) emulsion, in which an O/W emulsion is dispersed in an oil phase. W/O/W emulsion is more common than O/W/O emulsion. Double emulsion contains more interface and is even more thermodynamically unstable than single emulsion (Graaf et al. 2005).

Double emulsions have significant potential in many applications since, at least in theory, they

can serve as an entrapping reservoir for active ingredients that can be released from the inner phase to the outer phase by a controlled and a sustained mechanism. The major area of applications concerns the human pharmaceutical field: water-in-oil-in-water (W/O/W) emulsions have been investigated as potential vehicles for various hydrophilic drugs (vaccines, vitamins, enzymes, hormones) which would be then slowly released. Also, double emulsions have promising applications in other fields like the food industry (low calorie products, improved sensoric characteristics, taste masking), cosmetic industry (easily spreadable creams with encapsulated ingredients in both water and oil phases), separation science, and agriculture.

In practice, double emulsions are thermodynamically unstable systems with a strong tendency for coalescence, flocculation, and creaming. Most double emulsions consist of relatively large droplets, cannot withstand storage regimes, and have a strong tendency to release the entrapped matter in an uncontrolled manner. Four possible mechanisms are described for instability of W/O/W emulsion: (1) coalescence of the internal aqueous droplets, (2) coalescence of the oil drops, (3) rupture of the oil film separating the internal and external aqueous phases, and (4) passage of water (and water-soluble material, e.g., a drug) to and from internal droplets through the oil layer (Graaf et al. 2005). Much work has been devoted in the last decade in order to improve the stability of the multiple emulsions and the control of the release rates of the addenda. The most recent achievements are the use of polymeric emulsifiers to improve interface coverage and to better anchor into the dispersed phase and the decrease of droplet size by improving methods of formation (Garti 1997).

Double emulsion is generally prepared in a two-step emulsification process using two surfactants of opposite solubility. To produce O/W/O emulsion, a W/O emulsion is first prepared with a large excess of hydrophobic surfactant (HLB <10), by strong homogenization, to form the smallest possible droplets. In the second step a W/O/W double emulsion is further formed by gentle addition of the W/O (termed inner

emulsion) to water in which a hydrophilic one (HLB >10) has been dissolved (Bibette et al. 1999).

The most important conventional emulsification devices are stirring apparatuses, rotor–stator systems, and high-pressure homogenizers. **Membrane emulsification** is a relatively new method for the production of emulsions that has received increasing attention over the last 15 years. The technique is attractive given the low energy consumption, the better control of droplet size and droplet size distribution and especially the mildness of the process. **Microchannel emulsification** is a novel method for producing monodisperse emulsions. It is even more monodisperse than usually obtained with membrane emulsification (Graaf et al. 2005).

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Double Emulsion Production, Membrane Operations for

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Double emulsions are emulsions of emulsions. The droplets of the dispersed phase themselves contain even smaller dispersed droplets. Two main types of double emulsions are water-in-oil-in-water (W/O/W) emulsions and oil-in-water-in-oil (O/W/O) emulsions. The former is more common. Double emulsions have shown significant promise in the food industry, cosmetic industry,

pharmacology industry, and other fields like agriculture and separation science.

Double emulsions are usually prepared in a two-step emulsion process. First, internal emulsion (e.g., water-in-oil (W/O)) is designed under high-shear conditions to obtain small droplets. Secondary emulsion step for double emulsion (e.g., water-in-oil-in water (W/O/W)) is carried out with mild shear to avoid rupture of the internal droplets. Usually, the primary step can be produced by conventional method or also by membrane emulsification, while the membrane emulsification is especially suitable for the second emulsification step.

For the conventional emulsification method, the most commonly used devices are rotor–stator systems and high-pressure homogenizers. In rotor–stator systems (i.e., colloid mills), a high shear is generated between a rotor and a stationary smooth, roughened, or grooved surface. Turbulence is the primary cause of fluid disruption leading to the formation of droplets (Graaf et al. 2005). In a high-pressure homogenizer, the droplets are broken up in a nozzle by turbulence and cavitation. This process can be assisted with the use of an ultrasonic or electric fields. Due to their high throughput, rotor–stator systems and high-pressure homogenizers are suitable for large-scale production of emulsions. However, energy requirements of these systems are high because only a small part of the energy input is used for droplet breakup; most of the energy supplied is lost and converted into heat. Furthermore, shear stresses these systems applied may cause loss of functional properties of heat- and shear-sensitive components. In addition, they show poor control over droplet size and distribution.

In order to overcome the problems of traditional emulsification methods, a new technique for making emulsions known as “membrane emulsification” arouses people’s interest. This method involves using a low pressure to force the dispersed phase to permeate into the continuous phase through a membrane which has a uniform pore-size distribution. Droplets grow at pore outlets and then detach when reaching a certain size (Joscelyne and Tragardh 2000). One of the

most significant advantages of membrane emulsification is the low energy consumption. Also the better control of droplet size and distribution and the mildness of the process are highly attractive. Compared to conventional methods, a disadvantage of membrane emulsification is that the flux of the dispersed phase through the membrane is fairly low. However, the flux of dispersed phase could be increased by using a membrane with a low hydraulic resistance (e.g., microsieves).

The commonly used membranes for membrane emulsification are Shirasu porous glass (SPG) membranes, ceramic aluminum oxide (α -Al₂O₃) membranes, α -alumina- and zirconia-coated membranes, macroporous silica glass membranes, micro-fabricated metal membranes, polytetrafluoroethylene (PTFE) membranes, and hydrophobized silicon nitride microsieves.

For membrane emulsification two methods of operation are used: cross-flow membrane emulsification and premix membrane emulsification.

Generally, the important process controlling parameters are membrane pore size, porosity, thickness, and surface type, the velocity of continuous phase, the transmembrane pressure, and wall contact angle. It has been found that it is a linear relationship between the droplet size and membranes pore size. At high porosities, it is more likely for droplets to coalesce at the membrane surface before they detach. If the porosity is too low, the dispersed phase flux may be not sufficient for viable production of emulsions. The thinner the membrane, the larger the flux through the pores will be, which leads to a higher droplet expansion rate. It has been observed that hydrophilic membranes are fit for making O/W emulsions and hydrophobic membranes for W/O emulsions. The droplet size decreases sharply as the cross-flow velocity increases from rest and reaches a size where it becomes more or less independent of the flow velocity. The permeating flux is increased by increasing the transmembrane pressure. Another important parameter affecting the droplet size is the wall contact angle. Higher wall contact angle results in larger droplets and a more poly-disperse emulsion.

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Drinking Water Treatment

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Drinking water treatment includes the processes and operations applied in order to obtain an adequate and continuous supply of clear, colorless, odorless, palatable, and safe water.

The drinking water treatment requirements differ according to the feed water quality. Many aquifers and isolated surface waters are high in water quality and may be pumped from the supply and transmission network directly to any number of end uses, including human consumption. Source protection, i.e., conservation and protection of catchment areas, although not strictly in the category of treatment, can play a critical role in supporting the quality of water supplies (Sullivan et al. 2005). However, clean water sources are the exception in many parts of the world, particularly regions where the population is dense or where there is heavy agricultural use. In these places, the water supply must receive varying degrees of treatment before distribution (Peirce et al. 1998).

The most common water treatment process, known as conventional treatment, consists of coagulation, flocculation, sedimentation, filtration, and disinfection. Taken together, coagulation, flocculation, sedimentation, and filtration effectively remove many contaminants. Equally important, they reduce turbidity, yielding water of good clarity and hence enhanced disinfection efficiency. If not removed by such methods, particles may harbor microorganisms and make final disinfection more difficult. Generally, disinfection is

accomplished through the addition of an oxidant. Chlorine is by far the most common disinfectant used to treat drinking water, but other oxidants, such as chloramines, chlorine dioxide, and ozone, are also used. Although ultraviolet (UV) light can be used, it does not leave a residual, and usually a secondary disinfectant (i.e., chlorine) is added (Pepper et al. 2008).

In many cases, an additional treatment is necessary to remove suspended, colloidal, and dissolved constituents remaining after conventional treatment. Dissolved constituents may range from relatively simple inorganic ions, such as calcium, potassium, sulfate, nitrate, and phosphate, to an ever-increasing number of highly complex synthetic organic compounds (Tchobanoglous et al. 2003).

The ability of a water treatment facility to deliver a wholesome and high-quality product to its consumers usually occurs when advanced treatment methods are used. Activated carbon or granulated activated carbon (GAC) has been used to remove organic chemicals from water since the early 1900s. Ion exchange resins have been employed to remove inorganic metals for decades. Ozonation has been successfully used, instead of chlorine and bromine, to both disinfect water and oxidize organic constituents. Advanced oxidation processes have been used to remove persistent compounds. Ultraviolet light is being evaluated at a number of municipal treatment facilities for bacterial and viral control. Membrane separation processes are nowadays increasingly applied. As far back as 1985, the French have made use of membrane separation technology (i.e., reverse osmosis) for the removal of organic and inorganic compounds. Today, a number of reverse osmosis installations are operating worldwide to drinking water treatment. Reverse osmosis membranes can hold back a wide range of micropollutants including pesticides and pathogenic organisms and can replace the need for both ozonation and activated carbon filtration (Sullivan et al. 2005).

To produce fresh water from seawater and brackish water, desalination plants in industrial scale are nowadays installed throughout the world. Approximately one-half of the reverse osmosis (RO) systems currently installed are

used for desalinating brackish water or seawater (Baker 2012). Competing with RO, electrodialysis (ED) also plays an important role on the treatment of water in a very large market, a competition that is continuously intensified by the increased shortage of water resources. Both methods have advantages and disadvantages in drinking water treatment installations, and they have to be considered in order to choose the most optimal concept of membrane desalination.

Membrane fouling is one of the most important factors that limit greater use of desalination membranes. Fouling occurs due to particulate matter, organic matter, microorganisms forming biofilms, and inorganic scaling (Escobar 2010). Bacterial contamination problems have been reported as one of the main causes of membrane fouling in osmosis. This is caused by the characteristic of the membrane that serves as a barrier between the feed water and the product, which not only removes dissolved solids, but also bacteria, viruses, and insoluble substances. ED only removes ions. Therefore, any bacteria, colloidal material, or silica present in the feed water stream will remain in the product stream. This fact represents an advantage in terms of membrane fouling. On the other side, it can be seen as a major disadvantage, especially for the production of potable water, since microorganisms or organic contaminants are not eliminated.

By using ED technology, fouling can be minimized, thus decreasing the need for the addition of chemical products, by reversing the polarity of the system with electrodialysis reversal (EDR). By reversing the polarity (and the solution's flow direction) several times per hour, ions move in the opposite direction through the membranes, minimizing buildup. This generally minimizes membrane fouling, decreasing pretreatment requirements in comparison to RO (Seidel et al. 2011).

In general, electrodialysis reversal (EDR) is more attractive for the desalination of brackish water and in cases where the removal of organic matter and microbial control are not important. EDR is also of interest in treating brackish waters where silica is an important limitation (Escobar 2010). Nevertheless, the operating costs of

electrodialysis scale almost linearly in proportion to the salt concentration in the feed. Therefore, this technology is best suited to low-salt-concentration feed streams. Reverse osmosis costs also increase significantly with salt concentration but at a lower rate than electrodialysis does. The result is that reverse osmosis is the lowest-cost process for streams containing between 3,000 and 10,000 ppm salt. However, site-specific factors or plant size often make the technology the best approach for more dilute feed water or for streams as concentrated as seawater (35,000 ppm salt) (Baker 2012).

The salinity of brackish water is usually between 2,000 and 10,000 mg/L. The World Health Organization (WHO) recommendation for potable water is 500 mg/L, so up to 90 % of the salt must be removed from these feeds. Early RO cellulose acetate membranes could achieve this removal easily, so treatment of brackish water was one of the first successful applications of reverse osmosis. Several plants were installed as early as the 1960s. The osmotic pressure of brackish water is approximately 11 psi per 1,000 ppm salt, so osmotic pressure effects do not generally limit water recovery significantly. Limitations are generally due to scaling. Typical water recoveries are in the 70–90 % range, which means the brine stream leaving the system is up to ten times more concentrated in calcium, sulfate, and silica ions present in the feed. Disposal of the 10–15 % of the brackish water that remains as concentrated brine represents a significant problem. In fact, nowadays, brackish water desalination is the largest application of electrodialysis. The competitive technologies are ion exchange for very dilute saline solutions, below 500 ppm, and reverse osmosis for concentrations above 2,000 ppm. In the 500–2,000 ppm range, electrodialysis is often the low-cost process (Baker 2012). An advantage of electrodialysis compared to reverse osmosis is that a much higher brine concentration can be achieved, since there are no osmotic pressure limitations (Strathmann 2010). Typically 80–95 % of the brackish feed is recovered as product water. The degree of water recovery is limited by precipitation of insoluble salts in the brine (Baker 2012).

Seawater has a salt concentration of 3.2–4.0 %, depending on the region of the world. Because of this high salinity, only RO membranes with salt rejections of 99.3 % or more can produce potable water containing less than 500 ppm dissolved salt in a single pass. Application to seawater desalination of the first-generation cellulose acetate membranes, with rejections of 97–99 %, was limited. With the development of the polyamide hollow fine fibers and interfacial composites, suitable seawater membranes became available, and many plants have been installed. These membranes can produce permeate water that meets the WHO standard (<500 ppm salt) in a single pass or less than 200 ppm in a two-pass system, typically a single-stage seawater system and a single-stage brackish water system connected in series (Baker 2012).

Recently, membrane separation processes are being studied for the removal of emergent contaminants (e.g., pharmaceuticals and personal care products) from water. Surface and groundwater are the major renewable resources for sustainable drinking water production throughout the world. However, many chemical constituents that have not been considered historically as contaminants are present not only in wastewater, but also in natural waters at global scale. These emerging contaminants (EC) are commonly derived from municipal, agricultural, and industrial wastewater sources and pathways due to often inadequate treatment in conventional wastewater treatment plants, being detected in rivers downstream. In fact, the presence of EC can be expected in rivers, lakes, wells, and even drinking water. Considering that conventional water treatment with coagulation, sedimentation, and filtration achieves low levels of removal for EC, techniques that have been gaining attention in the past few years are pressure-driven membrane processes nanofiltration (NF) and reverse osmosis (RO). These two treatments seem to be able to effectively remove most organic and inorganic compounds and microorganisms from raw water, and their application in drinking water treatment has been seen as preferred alternatives for the removal of emerging organic contaminants (Quintanilla 2010; Radjenović et al. 2008).

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Droplet Size

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Droplet size is defined by the diameter of an equivalent sphere having the same property (such as volume or mass) as the analyzed droplet. In order to simplify the interpretation of particle size distribution data, a range of statistical parameters can be opportunely selected for any given sample. The most common droplet size in a droplet size distribution could be reported as:

- Mean: average size of a population
- Median: size where 50 % of the population is below/above
- Mode: size with highest frequency

There are many different means that can be defined depending upon how the droplet size distribution is analyzed. The three most commonly used for particle sizing are:

- Surface area mean $D[3, 2]$ (Sauter mean diameter)

It is the weighted average surface diameter, assuming spherical particles of the same surface area as the actual particles:

$$D[3, 2] = \frac{\sum D_i^3 n_i}{\sum D_i^2 n_i}$$

It is most relevant where specific surface area is important, e.g., bioavailability, reactivity, and dissolution. It is most sensitive to the presence of fine droplets in the size distribution.

- Volume moment mean $D[4, 3]$ (De Brouckere mean diameter)

It is the weighted average volume diameter, assuming spherical particles of the same volume as the actual particles:

$$D[4, 3] = \frac{\sum D_i^4 n_i}{\sum D_i^3 n_i}$$

It is relevant for many samples as it reflects the size of those particles which constitute the bulk of the sample volume. It is most sensitive to the presence of large particulates in the size distribution.

- Number length mean $D[1, 0]$

It is often referred to as the arithmetic mean:

$$D[1, 0] = \frac{\sum D_i n_i}{\sum n_i}$$

It is most important where the number of particles is of interest, e.g., in particle counting

applications. It can only be calculated if we know the total number of particles in the sample and is therefore limited to particle counting applications.

For volume-weighted particle size distributions, such as those measured by laser diffraction, diameter is reported based upon the maximum particle size for a given percentage volume of the sample. The most common diameters are the Dv10, Dv50, and Dv90 that are corresponded to 10, 50, and 90 vol% on a relative cumulative droplet size curve, respectively.

Drug Delivery by Membrane Operations

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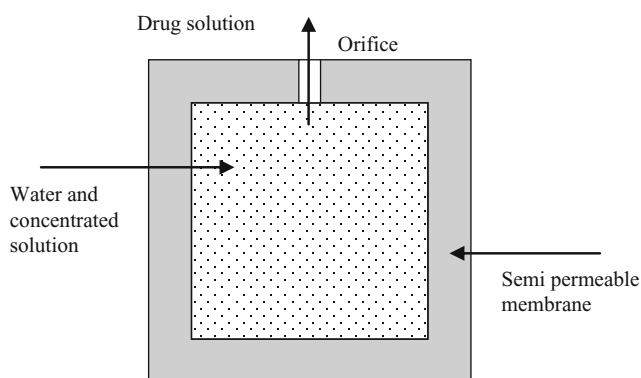
Drug delivery is a field of vital importance to medicine and healthcare. A drug delivery system is a formulation or a device that enables the introduction of a therapeutic substance in the body and improves its efficacy and safety by controlling the rate, time, and place of its release (Jain 2008). It includes the administration of the therapeutic product, the release of the active ingredients by the product, and the subsequent transport of the active ingredients across the biological membranes to the site of action. A drug delivery system may be (1) a device used to deliver the drug or (2) a formulation of the drug which will be administered for a therapeutic purpose. Drugs may be introduced into the human

body by various anatomical routes. The choice of the route of administration depends on the disease, the effect desired, and the product available. Drugs may be administered directly to the organ affected by the disease or given systemically and targeted to the organ. Methods of systemic drug delivery are classified as follows: gastrointestinal system (oral, rectal), parenteral, transnasal, pulmonary (drug delivery by inhalation), transdermal, and intraosseous infusion. The oral route of drug administration is the most used for both conventional as well as novel drug delivery. The reasons for this preference are the ease of administration and widespread acceptance by patients.

Membrane devices used to deliver the drug consist basically of a drug reservoir (Stamatialis et al. 2008). Two main types of systems can be distinguished: (1) osmotic membrane systems and (2) diffusion-controlled membrane systems. An osmotic system consists of a reservoir made of a polymeric membrane permeable to water but not to the drug (semipermeable membrane) Fig. 1. The reservoir contains a concentrated drug solution. As water crosses the membrane due to osmotic pressure, the drug solution is released through the orifice. In diffusion-controlled membrane systems, the drug release is controlled by transport of the drug across a membrane. The transport is dependent on the drug diffusivity through the membrane and the thickness of the membrane. These systems find broad application in pills, implants, and patches (see Drug-Delivery Applications).

Membrane-based formulations used to deliver the drug consist of carriers that are biodegradable, biocompatible, targeting, and stimulus responsive

Drug Delivery by Membrane Operations,
Fig. 1 Schematic view of an osmotic drug delivery system



like liposomes and nanocapsules (Zhang et al. 2013). Liposomes are enclosed spherical vesicles that are organized in one or several concentric phospholipid membrane bilayers with an aqueous phase inside. Liposomes can entrap hydrophilic pharmaceutical agents in their internal aqueous compartment and lipophilic drugs within the lipid membrane. Nanoparticles (nanospheres and nanocapsules) are ranging in size from about 10 to 1000 nm. Nanospheres have a matrix type structure with drugs adsorbed at their surface, entrapped in the particle, or dissolved in it. Nanocapsules have a polymeric shell membrane and an inner liquid core, the drugs being dissolved in the inner core or adsorbed at their surface. Nanoparticles have been investigated for the entrapment of a wide variety of drugs, for applications ranging from ophthalmic delivery to carriers in chemotherapy.

Cross-Reference

► Drug Release

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Drug Delivery, Application of

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Drug delivery membrane systems include osmotic membrane systems, diffusion-controlled membrane systems (pills, implants, patches), and

transdermal drug delivery (passive diffusion, iontophoresis, and skin or device-controlled delivery) (Grassi 2009). These drug delivery applications concern mainly transdermal, oral, and ocular delivery routes of administration.

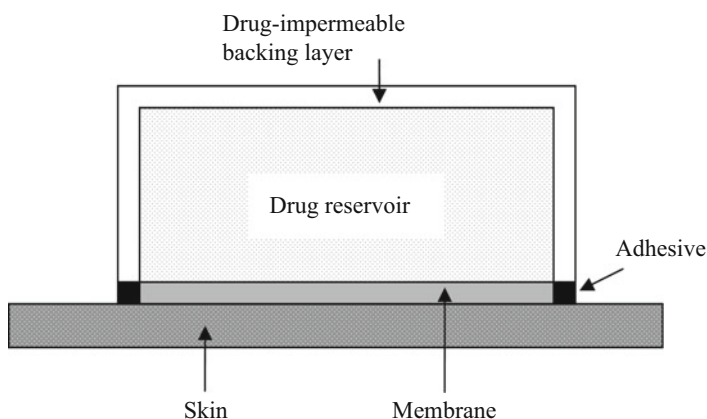
In transdermal drug delivery (Stamatialis et al. 2008), the drug is incorporated into a patch and delivered through the skin due to the concentration difference or electrical current (Fig. 1). Transdermal patches are used as a convenient and effective method of drug delivery through the human skin. A membrane may exclusively control or partially control drug transport together with other components (such as the adhesive layer). Patches are commercialized, for example, for delivery of nicotine for smoking cessation, estrogen or testosterone for hormonal therapy, and methylphenidate for attention-deficit/hyperactivity disorder. Ocular patches are membrane-controlled reservoir systems. The drug, accompanied by carriers, is captured in a thin layer between two transparent, polymer membranes, which control the rate of drug release. The device is placed on the eye where it floats on the tear film. The drug slowly diffuses to the target area.

As a noninvasive transdermal drug delivery method, iontophoresis applies electrical current to deliver drugs through the skin to the underlying tissue or capillaries and then to the whole circulating system (Fan et al. 2008). A voltage applied between two electrodes immersed in a drug solution causes the drug to be moved from the donor part into the skin. The positively charged electrode (anode) attracts the negatively charged drug ions; the negatively charged electrode (cathode) attracts the positively charged ions. These devices are commercialized for example for delivery of lidocaine and epinephrine in local analgesia.

In oral delivery, the drug is pressed into a tablet which is coated with a nondigestible hydrophilic membrane such as cellulose esters like cellulose acetate, cellulose acetate butyrate, cellulose triacetate, and ethyl cellulose (Stamatialis et al. 2008; Grassi 2009). Once the membrane gets hydrated, a viscous gel barrier is formed, through which the drug slowly diffuses. The release rate of the drug

Drug Delivery, Application of,

Fig. 1 Schematic view of transdermal membrane delivery systems



is determined by the type of membrane used. The key feature of these systems is that drug release is independent of pH and hydrodynamics of the external dissolution medium. The result is a robust dosage form for which the *in vivo* rate of drug release is comparable to the *in vitro* rate, producing an excellent *in vitro/in vivo* correlation. Another key advantage is that they are applicable to drugs with a broad range of aqueous solubility such as diltiazem HCl, carbamazepine, metoprolol, oxprenolol, nifedipine, and glipizide.

Another example is implants which consist of a membrane reservoir containing a drug in liquid or powder form (Grassi 2009). The drug slowly diffuses through the nondegradable membrane that usually consists of silicone and ethylene-co-vinyl acetate. By properly choosing membrane thickness and permeability, release kinetics can be controlled and designed for a specific therapeutic target. For example, an implantable 5-year contraceptive permits the long-term release of levonorgestrel.

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Drug Permeability

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An important property of a drug is its bioavailability. For an orally administered drug, the bioavailability is mainly limited by its solubility and permeability through the intestinal epithelia. It is therefore important to have access to drug permeability. Today the most often used methods are the Caco-2 model and the parallel artificial membrane permeation assay (PAMPA).

Caco-2 cells are human colon epithelial cancer cell lines used as a model of human intestinal permeation of drugs and other compounds (van Breemen and Li 2005). When cultured as a monolayer, Caco-2 cells differentiate to form tight junctions between cells to serve as a model of paracellular movement of compounds across the monolayer. Caco-2 cell monolayers are usually cultured on semipermeable plastic supports that may be fitted into the wells of multi-well culture plates. Test compounds are then added to either sides of the monolayer. After incubation, aliquots of the solution in opposite chambers are removed for the determination of the concentration of test compounds. The apparent permeability coefficients are then calculated. Radiolabeled compounds used in the original Caco-2 cells monolayer assays have been replaced by the use of liquid chromatography mass spectrometry

(LC-MS) and LC-tandem mass spectrometry (LC-MS-MS). MS eliminates the need for radiolabeled compounds and permits the simultaneous measurement of multiple compounds.

The parallel artificial membrane permeability assay (PAMPA) is a possible low-cost alternative to cellular models (Avdeef 2005). Its popularity in the industry has risen rapidly. On the contrary to cell-based permeation assays, PAMPA assay contains artificial membrane that is used for evaluating the permeation properties of the compound. The system consists of phospholipid layer on a filter plate, half of which is treated with an organic solvent, mimicking the cell membrane. Various models with different lipids and/or organic solvent (hexadecane/dodecane) are used. Due to its artificial nature, PAMPA model predicts only passive permeation. When used in parallel with cell-based in vitro permeation assays (Caco-2), the differences in the results can reveal other than passive permeation mechanisms. PAMPA is suitable for high-throughput evaluation of passive permeation characteristics at multi-well culture plates, classifying compounds to high or low permeation. PAMPA assay can also be conducted at several physiologically relevant pH conditions (2–8), to see the effect of ionization of the compound to its passive permeation.

Another recent alternative to access to drug permeability properties is the phospholipid vesicle-based permeation assay (PVPA) developed for measurement of passive drug permeability (Fischer et al. 2011). The system consists of a tight layer of liposomes on a filter support which is obtained by first depositing smaller liposomes that will go into the pores and then larger liposomes that will layer on top of the filter, by use of centrifugation. Freeze-thaw cycling is then used to promote liposome fusion to generate a tight barrier used for permeability measurement. The characterization of the barrier structure showed that the pores of the filter are filled with liposomes and that there is a layer of liposomes on top of the filter.

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Drug Release

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Polymeric systems are often used to provide controlled release and protect the drug from biological degradation prior to its release. The development of these devices started with the use of nonbiodegradable polymers, which rely on the diffusion process, and subsequently progressed to the use of biodegradable polymers, in which swelling and erosion take place. Based on the physical or chemical characteristics of polymer, drug release mechanism from a polymer matrix can be related to three main mechanisms (Arifin et al. 2006):

- Drug diffusion from the non-degraded polymer (diffusion-controlled system).
- Enhanced drug diffusion due to polymer swelling (swelling-controlled system).
- Drug release due to polymer degradation and erosion (erosion-controlled system). Diffusion is involved in the three systems. For a nonbiodegradable polymer matrix, drug release is due to the concentration gradient by either diffusion or matrix swelling (enhanced diffusion). For biodegradable polymer matrix, release is controlled by the hydrolytic cleavage of polymer chains that lead to matrix erosion, even though diffusion may be still dominant when the erosion is slow.

Empirical and semiempirical mathematical models are often used to describe drug release from matrix-based drug delivery systems

(Siepmann and Peppas 2012). The most popular mathematical equation to describe the release rate of drugs from matrix systems is the Higuchi's equation (Higuchi 1961). Initially valid only for planar systems, it was later modified and extended to consider different geometries and matrix characteristics including porous structures. The equation of the Higuchi model is given as:

$$\frac{M_t}{A} = \sqrt{D(2c_0 - c_s)c_s t} \text{ for } c_0 > c_s \quad (1)$$

where M_t is the cumulative absolute amount of drug released at time t , A is the surface area of the controlled release device exposed to the release medium, D is the drug diffusivity in the polymer carrier, and c_0 and c_s are the initial drug concentration and the solubility of the drug in the polymer, respectively. Equation 1 can be expressed as:

$$\frac{M_t}{M_\infty} = K\sqrt{t} \quad (2)$$

where M_∞ is the absolute cumulative amount of drug released at infinite time (which should be equal to the absolute amount of drug incorporated within the system at time $t = 0$) and K is a constant reflecting the design variables of the system. Thus, the fraction of drug released is proportional to the square root of time. Alternatively, the drug release is proportional to the reciprocal of the square root of time.

Another commonly used semiempirical equation to describe drug release from polymeric systems is the power law:

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\delta^2}\right)^{1/2} \left(\pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{erfc} \frac{n\delta}{2\sqrt{Dt}} \right) \quad (3)$$

where M_t and M_∞ are the absolute cumulative amount of drug released at time t and infinite time, respectively; k is a constant incorporating structural and geometric characteristics of the device; and n is the release exponent, indicative of the mechanism of drug release. The classical Higuchi equation (Eq. 1) represents the special

case of the power law where $n = 0.5$. The power law describes in many cases dynamic swelling and drug release from glassy polymers.

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Dry Spinning

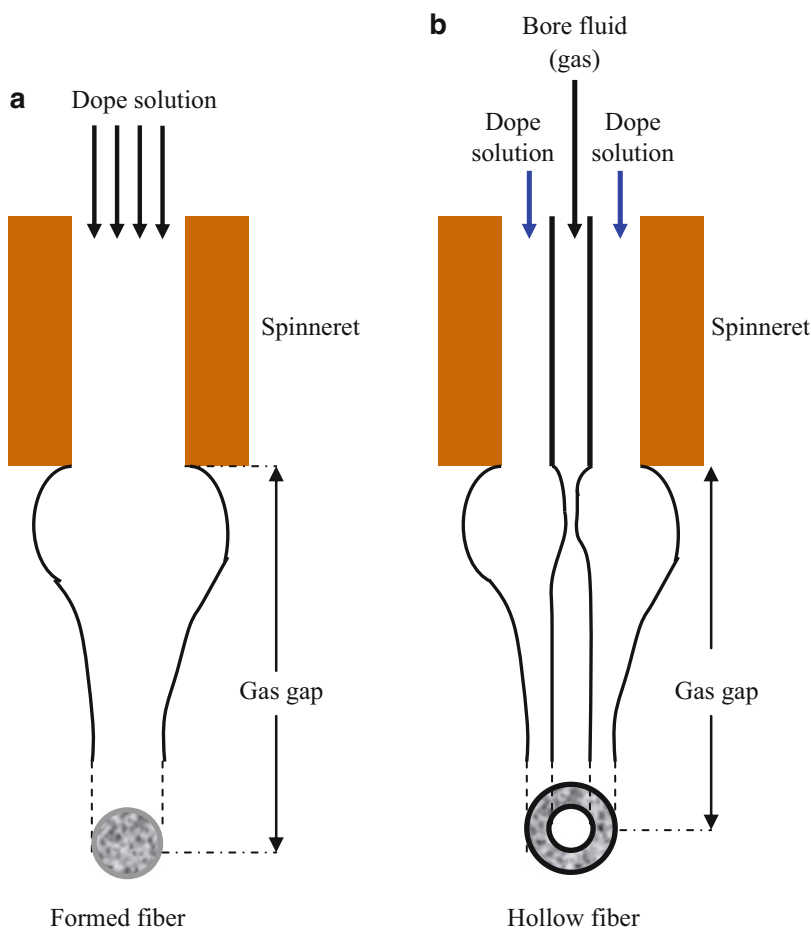
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Dry spinning is an extrusion technique used for fabrication of fibers (filaments) or hollow fibers using a viscous dope solution containing polymer (s) dissolved in a volatile solvent or in a solvent mixture with a high volatility. The dope solution is pumped (extruded) through a filter and then through a spinneret or tiny orifices (i.e., jets) in a heated drying chamber. As the dope solution exit the spinneret, air or an inert gas is used to evaporate the solvent(s) so that the fiber solidifies and collected on a take-up wheel. Spinning is followed by stretching of the as-spun fibers to orient the polymer chains along the gas gap (fiber axis). In dry spinning the as-spun fibers do not come in contact with any precipitating liquid (bore liquid, external coagulant). Dry spinning differs from dry/wet spinning and wet spinning in that the solidification is achieved through evaporation of the solvent carried out by a stream of air or an inert gas. In dry spinning and melt spinning, the dimensions of the spinneret are not so crucial because the fiber dimensions are mainly determined by the ratio of the extrusion rate and

Dry Spinning,

Fig. 1 Schematic presentation of die swell occurring in the nascent fiber (a) and hollow fiber (b) when extruded from a spinneret



“tearing rate” (Mulder 1992). The gas flow used for solvent evaporation and solidification of the fibers influences to a significant extent the quality of the produced fibers. In dry/wet spinning and wet spinning, precipitating liquids are involved (bore liquid, external coagulant). In dry spinning, the fiber does not need to be dried like in wet spinning and dry/wet spinning. Examples of polymer used for production of fibers by dry spinning are cellulose acetate, polyacrylonitrile, polyurethane, and fibers based on poly-m-phenylene isophthalamide, polybenzimidazoles, polyamidoimides, and polyimides. In general, dry spinning is used for polymers that cannot be used in melt spinning. The concentration of the spinning dope solution and the spinning speeds is higher than those used in dry/wet spinning and wet spinning. Spinning speeds range between

300 and 1000 m/min. The spinning rate in melt spinning (thousands of meters per minute) is much higher than that used in the dry/wet spin technique (meters per minute) (Mulder 1992).

When a polymer solution is extruded through a tube in orifice spinneret, shear stress is induced within the spinneret (Fig. 1) (Khayet and Matsuura 2011). There are at least three forces (stresses) applied upon the dope solution: (i) shear and elongation stresses within the spinneret, (ii) gravity induced by the weight of the spun hollow fiber, and (iii) stress induced by the take-up system (i.e., wind-up drum or take-up wheel). It is known that the stress affects dramatically the polymer molecular orientation and relaxation at the outer surface of the nascent fiber. The effects of elongation and relaxation after exiting from the spinneret will play

important roles on final hollow fiber structure. Furthermore, the induced elongation stresses outside the spinneret from gravity through the air gap complicate the kinetics and dynamics of the phase inversion process. In addition, non-Newtonian polymer solutions may exhibit die swell and relaxation after exiting from spinneret.

Molecular chains tend to align themselves much better, and this enhanced orientation causes the polymer molecules to pack closer to each other leading to a tighter skin fiber structure. The molecular orientation induced by shear stress within the spinneret might relax in the air gap region, before reaching the take-up wheel, if the elongation stress along the spin line is small as spinning dope solution is a viscoelastic fluid or might be enhanced if the spin line stress is high. In other words, the elongation stress caused by gravity along the spinning line becomes more pronounced with increasing the distance between the spinneret or jets and the take-up wheel.

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DSP&DE Model Applications

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DSP&DE Model Applications

The applications of the Donnan/steric pore (DSP) and dielectric exclusion (DE) model (known as the SEDE model in literature) can be summarized as follows:

- (i) To characterize a *nanofiltration* (NF) membrane in terms of the average pore radius (r_p); the effective membrane thickness (δ); the

volume charge density (X), which is defined as the number of moles of fixed charges per unit of pore volume; the dielectric constant of the solution inside pores (ϵ_p); and the dielectric constant of the membrane material (ϵ_m)

Characterization using uncharged solutes:

r_p and δ are usually determined by the analysis of rejection data of neutral solutes (Bowen et al. 1997; Schaep et al. 1999; Labbez et al. 2002) since in that case the rejection only depends on structural parameters. Estimation of r_p and δ with various uncharged solutes shows that the variation in r_p for best fit is relatively small. Hence, a mean value of r_p can be considered. However, it is reported that the parameter δ varies significantly with solute size (Bowen et al. 1997; Schaep et al. 1999; Labbez et al. 2002). For an unknown solute, δ can then be obtained from a correlation between δ and r_i/r_p , r_i being the solute radius (Bowen et al. 1997). It was also found that the values of δ obtained from the fitting of the rejection data are different from that determined from water permeability measurements by using the Hagen-Poiseuille equation (Bowen et al. 1997; Labbez et al. 2002). As the quality of fitting obtained with an independent fit of both r_p and δ is much less good than that obtained using δ from permeability data, some authors recommend that the value of δ is not estimated from the permeability data for NF membranes.

Characterization using single-salt solutions:

The description of experimental rejection rates is in general satisfactory, and the fitted values of X appear to be physically reasonable when calculations are performed by neglecting DE mechanisms, i.e., by using the DSP model (based on a Donnan/steric exclusion mechanism). The analysis of rejection data shows that X is not constant but depends very much on the salt nature and its concentration. The increase in the

volume charge density with the salt concentration is probably caused by interactions between free ions in solutions and the membrane, where each individual ion contributes to the membrane charge by means of adsorption. However, the DSP model fails to describe the high rejection rates observed with some NF membranes in the case of solutions containing divalent counterions (Vezzani and Bandini 2002; Szymczyk and Fievet 2005). Indeed, the use of the DSP model leads to the prediction of unrealistic high volume charges or to a change of the sign of the membrane charge (which is not supported by streaming potential measurements) (Szymczyk and Fievet 2005) or to a ratio of the volume charge density to the salt concentration increasing with concentration (which disagrees with common adsorption isotherms) (Bowen and Welfoot 2002) or to the increase of the rejection rate as the membrane charge density X decreases (which is the opposite behavior from the one predicted by the *Donnan*/steric exclusion mechanism). This suggests that additional phenomena have to be accounted for so as to provide a better understanding, characterization, and prediction of NF membrane performances. However, it should be mentioned that the DSP model was proved to provide a coherent description of NF behavior for membranes at the borderline between UF and NF (membranes with larger pores and very thick active layers) as has been shown, e.g., in Lefebvre (2003) and Lefebvre et al. (2004) for ion rejection and filtration potential (i.e., the pressure-induced potential arising across membranes containing selective layers).

The DSP&DE model was shown to provide a rather good description of the rejection properties of both symmetric (KCl) and asymmetric (MgCl_2 , CuCl_2 , ZnCl_2 , NiCl_2 , CaCl_2) single-salt solutions by negatively charged organic membranes (AFC 30 and AFC 40 PCI NF

membranes) (Szymczyk and Fievet 2005; Szymczyk et al. 2007) with physically realistic values of ε_p (i.e., ranging from 42 to 69). However, literature shows that the approaches used to obtain a good agreement between theory and experiment differ depending on the couple membrane/salt studied. The description can be satisfactory considering (a) all exclusion mechanisms (Szymczyk and Fievet 2005; Szymczyk et al. 2006, 2007), or (b) steric, electric, and Born dielectric exclusion mechanisms (Cavaco Morão et al. 2008; Bouranene et al. 2009), or (c) steric, electric exclusion mechanisms and image forces (Bandini and Vezzani 2003; Bouranene et al. 2009).

Characterization using multi-ionic solutions:

In the case of 3-ion solutions, different approaches of the DSP&DE model have also to be used to appropriately describe the separation properties (Bouranene et al. 2009; Szymczyk et al. 2006). Unlike the results obtained with 2-ion and 3-ion solutions, the four exclusion mechanisms (*Donnan*, steric, Born, and image effects) are found to be unable to describe the experimental data in the case of solutions containing more ions. However, the description of the experimental rejection rates is quite satisfactory considering either Born dielectric effect or image forces (in addition to steric and electric exclusion mechanisms).

The application of the DSP&DE model was also extended to a complex solution of five ions (K^+ , Cl^- , NH_4^+ , SO_4^{2-} , and clavulanate ion), which mimics the industrial NF feed in the isolation process of clavulanate, which is a pharmaceutical product (Cavaco Morão et al. 2008). With a single-fitted parameter ε_p and considering that the ion selectivity is governed by *Donnan*, steric, and Born dielectric exclusion mechanisms, a good agreement was obtained between the

calculated rejections rates of the five ions and experimental values.

- (ii) To investigate the exclusion mechanisms in NF

The coupling between the various mechanisms involved in the ion rejection could be investigated. It was shown, e.g., that dielectric effects (i.e., Born dielectric effect and image forces) make the *Donnan* exclusion stronger. Indeed, unlike *Donnan* exclusion, image forces and Born dielectric effect do not differentiate (qualitatively) between coions and counterions since they are controlled by the square of the ion charge. As a result, both coions and counterions are excluded from pores by image forces. By decreasing the internal concentration, the dielectric exclusion phenomenon therefore reduces the screening of the membrane fixed charge and thus strengthens the electric exclusion. By contrast, the presence of a fixed charge on the pore walls as well as the ionic atmosphere surrounding an ion screens the interaction of this ion with the pore wall via image forces. The coupling between electric and dielectric exclusion mechanisms may result in a non-monotonous variation of the rejection with membrane charge density (X). It was also shown that the Born effect also strengthens the contribution of image forces.

The analysis of the rejection properties of a ternary ion mixture by an amphoteric ceramic membrane (Szymczyk et al. 2006) has shown that the dielectric constant inside the pores ϵ_p (which was fitted to experimental rejection rates) decreases with increasing normalized volume charge density (defined as the ratio of the membrane volume charge density to the total charge concentration in solution), which means that the presence of fixed charges at the pore walls (in addition to the confinement effect) could also have an influence on the orientation of solvent dipoles.

The DSP&DE model (more exactly the DSP model) was also applied to mixtures of uncharged solutes and ions in order to

investigate the significance of dehydration and pore swelling phenomena on the NF of neutral solutes, which could be responsible for the observed decrease in the neutral solute rejection in the presence of salts (Escoda et al. 2013). To this end, rejection properties of two NF ceramic and polymeric membranes were studied with single polyethylene glycol (PEG) solution and mixed PEG/inorganic electrolyte solutions. Rejection data obtained with the ceramic membrane (rigid pores) were used to compute the dehydration of the PEG molecules induced by the surrounding ions. Concerning the polymeric membrane, the decrease in the rejection rate was found to be systematically higher than for the ceramic membrane. The additional decrease was then ascribed to the swelling of the pores. The experimental data of rejection rates were then used to compute the variation in the mean pore radius in the presence of the various salts. For the two membranes, it was found that the contribution of the dehydration effect follows the Hofmeister series (Kunz 2004).

- (iii) To predict the rejection properties of a NF membrane

It must be stressed that accounting for the dielectric exclusion mechanism inevitably increases the number of fitting parameters, making the use of the DSP&DE model less appropriate for predictive purposes. Notably, the dielectric constant of the solution confined inside the membrane pores (ϵ_p) is used as a fitting parameter in all current versions of the DSP&DE model (Szymczyk and Fievet 2005, 2006, 2007; Escoda et al. 2011; Cavaco-Morao et al. 2008). Indeed, although in principle ϵ_p could be determined from dielectric relaxation measurements, in practice, the measurement of this parameter is extremely difficult due to (a) the multilayer (thick support layers) and composite (membrane material and confined solution) structure of NF membranes and (b) the pore size distribution. It must also be pointed out that the multilayer/composite structure and nanodimensional

pores make also the determination of the membrane charge density extremely difficult. Finally, unlike the DSP model, the prediction of membrane performances for multi-ionic systems by means of the adjustable parameters obtained for single-salt solutions is not possible with the DSP&DE model. Indeed, the choice for X and ϵ_p (ϵ_m being assumed to be known) allowing the description of experimental rejection rates is not unique for single-salt solutions because both electric exclusion and dielectric exclusion contribute to reject ions.

Cross-References

► Nanofiltration

References

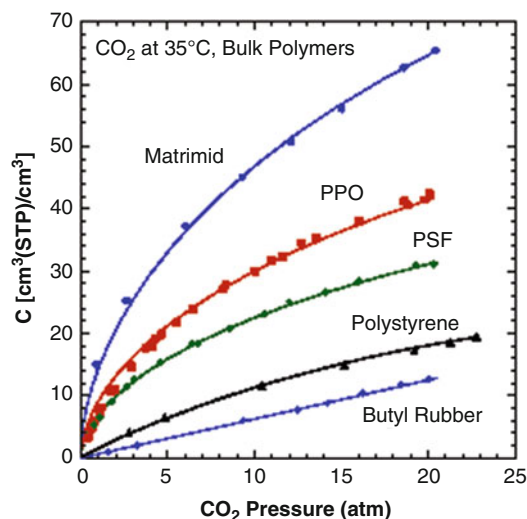
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Dual Mode Sorption Model

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The **dual mode sorption model** is a convenient and commonly used equation for describing gas sorption in polymers at temperatures below the glass transition temperature, T_g , of the polymer. Gas sorption in glassy polymers generally (a) exhibits nonlinear isotherms that are concave to the pressure axis, unlike the linear ones seen above T_g , (b) shows greater levels than for rubbery polymers with the extent being larger the higher is the T_g , and (c) depends on the prior history of the sample and the details of the measurement protocol (Horn and Paul 2012). The first two aspects are well illustrated in Fig. 1 that shows the concentration of carbon dioxide, C , dissolved in five different polymers as a function



Dual Mode Sorption Model, Fig. 1 Sorption isotherms for CO₂ in various polymers at 35 °C (Reprinted with permission from Horn and Paul 2012. Copyright 2012 American Chemical Society)

of the pressure, p , in the external carbon dioxide gas phase. Butyl rubber shows a linear isotherm, while all four of the glassy polymers show features (a) and (b) mentioned above at this measurement temperature, i.e., $T = 35$ °C. The extent of carbon dioxide sorbed into these glassy materials increases the higher is the T_g ; i.e., their glass transition temperatures descend in the following order: 310 °C for the polyimide Matrimid 210 °C for poly(phenylene oxide) (PPO) 186 °C for polysulfone (PSF) 100 °C for polystyrene.

The dual mode sorption model consists of the sum of Henry's law term and a Langmuir term, i.e.,

$$C = k_D p + \frac{C'_H b p}{1 + b p} \quad (1)$$

where k_D is Henry's law coefficient, C'_H is the Langmuir capacity term, and b is an affinity parameter. It appears that Barrer et al. (1958) were the first to propose this now well-known equation. Equation 1 provides a very good fit of data like that in Fig. 1 where the C'_H obtained by the fitting would increase as the polymer T_g increases relative to the measurement

temperature T , i.e., $C'_H \sim T_g - T$, and is thought to be related to the unrelaxed volume of the glass; see Paul (2010) for a recent summary of the extensive literature in this area. The C'_H term would be zero for butyl rubber, i.e., Eq. 1 reduces to Henry's law, since it is not in the glassy state.

Petropoulos (1970) proposed that the Langmuir population may have a finite, but different, mobility than Henry's law population. Paul and Koros (1976) extended this analysis to give expressions for the time lag and the following expression for the permeability coefficient, P , for gases in glassy polymers:

$$P = k_D D_D + \frac{C'_H b D_H}{1 + b p_2} \quad (2)$$

where D_D is the diffusion coefficient associated with Henry's law population and D_H is the diffusion coefficient for the Langmuir population and p_2 is the upstream pressure of the permeating gas. This has become known as the **dual mobility model**. It predicts that the permeability decreases slightly as the upstream pressure increases and this is what is commonly observed experimentally in simple cases where the polymer is not plasticized significantly by the permeating gas.

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Durability of Membrane (Lifetime of Membrane)

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Durability (or lifetime) of membranes is a critical factor in the commercialization potential of any membrane material, as it must be resilient to the process conditions over an extended period of time. The lifetime of a membrane is also an important factor in the economic evaluation of a membrane process, as replacement of membranes is a significant cost burden.

A range of factors influence the durability of membrane materials. These include chemical degradation of either the active layer or support structure due to harsh chemical components in the feed stream, for example, feeds with low or high pH conditions, as well as high electrolyte concentrations, polymeric aging, and polymer plasticization, leading to increased probability of the active layer rupturing. An example of this is cellulose acetate membranes being plasticized by exposure to hydrocarbons in petrochemical gas separation applications; active layer compaction due to the extended exposure to high-pressure differentials across the membrane, resulting in reduced flux because of loss in diffusivity; and membrane fouling, which is the buildup of foreign matter on a membrane's surface resulting in decreased performance. An example is microbial growth in water treatment. Finally, mechanical abrasion of the active and support layers is caused by particulate matter being present in system. Each of these factors influences membrane materials differently, depending on the application.

There are a number of approaches to extend membrane lifetimes, most of which focused on overcoming membrane fouling. These include feed pretreatment, chemical and mechanical cleaning, feed stream pulsation, and pressure variation, as well as chemical additives to prevent

fouling in the first place. These techniques can extend a membrane module's lifetime but will not address issues such as chemical degradation, polymeric aging, and mechanical abrasion. Hence, all membrane modules' separation performances decrease over time in all industrial processes and replacement is necessary.

Currently, the industry standard is for a membrane module lifetime of ~5 years under standard process conditions (Li et al. 2008). For the majority of reverse osmosis membrane plants currently being commissioned or under construction, the RO membranes are guaranteed by the manufacturer for 5 years. Similarly, vapor separation membranes in the petrochemical industry have a lifetime of 3–5 years, dependent on the conditions of the feed. Seawater ultrafiltration membranes last up to 7 years because of their resilient material and the ability to avoid regular chemical cleans. Alternatively, dairy and brine processing membranes need to be replaced every year because of biological and particulate buildup, while hemodialysis and hemofiltration membranes are only required to function for a few hours, as they are single-use only equipment.

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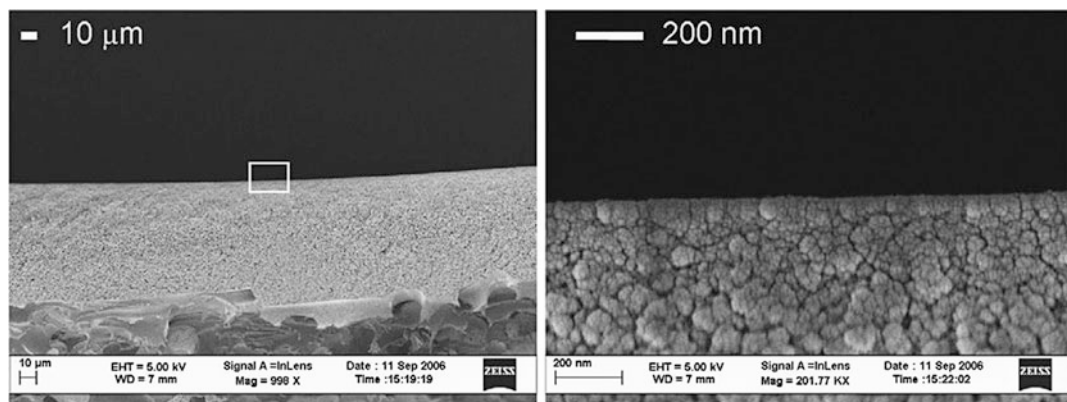
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DuraMem™ Membrane

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DuraMem™ is a range of highly stable organic solvent nanofiltration (OSN) membranes manufactured by Evonik – Membrane Extraction Technology Ltd. (www.duramem.evonik.com). Membranes are of integral asymmetric type and are based on cross-linked polyimide (PI) (Great Britain 2007; Toh et al. 2007). These membranes



DuraMem™ Membrane, Fig. 1 A typical SEM micrograph of a cross section (*left*) and top separating layer (*right*) of cross-linked PI membranes (Adapted from Toh et al. (2007))

are available in formats of flat sheets and spiral-wound membrane modules within different molecular weight cutoff range ($150\text{--}900\text{ g mol}^{-1}$) and possess excellent stability in most of the organic solvents including polar aprotic solvents such as dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP). The membranes have a spongelike structure (Fig. 1) and are usable in acetone, ethanol, methanol, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, dimethylacetamide, isopropanol, acetonitrile, methyl ethyl ketone, ethyl acetate, and others (www.duramem.evonik.com). The membranes have been operated continuously for 120 h in DMF and THF and showed stable fluxes and good separation performances, with DMF permeability in the range of $1\text{--}8 \times 10^{-5}\text{ Lm}^{-2}\text{h}^{-1}\text{Pa}^{-1}$ ($1\text{--}8\text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) (Toh et al. 2007). Possible re-imidization and loss of cross-linking at elevated temperatures limit their range of application to temperatures $<50\text{ }^{\circ}\text{C}$. The membranes can be operated in a pressure range of 20–60 bar (290–870 psi).

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Dusty-Gas Model (DGM)

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The Dusty-Gas Model is a transport model describing the motion of fluid mixtures through porous media. Its particular name is due to the main hypothesis behind its development: in a multicomponent system of n gas species moving within a porous medium, the porous medium itself is viewed as an additional $(n + 1)$ -th component of the mixture, consisting of giant molecules (or dust particles) constrained to remain fixed in the space by the presence of a virtual external force. However, if this virtual external force is removed, the model can be also used to describe motion of aerosols.

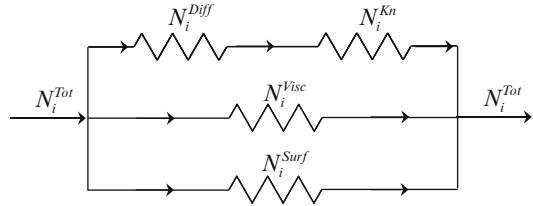
This model has been independently reinvented several times in the course of the history, starting with James Clerk Maxwell in 1860 (Maxwell 1980). However, it was only in 1983 that it was formalized as a mature theory by Mason and Malinauskas (1983), who described in detail the number of different hypotheses leading to corresponding different expressions of the model.

The Dusty-Gas Model is particularly important in *Membrane Technology*, as it can be used to describe the transport of a multicomponent fluid mixture through porous membranes and/or porous supports. Its use is not restricted to just ideal gases, but it can apply to real fluids as well, requiring the use of activities instead of partial pressures.

The model takes into account the following concurrent and independent transport modes:

- Knudsen flow (i.e., free-molecule flow), where the molecule-wall collisions are dominant over the molecule-molecule ones, so that the latter can be neglected.
- Continuum diffusion, where the species in mixture move with respect to each other by the effect of chemical potential gradient, which can include diffusion driven by concentration gradient, temperature gradient, and/or by external forces. In this case, the molecule-molecule collisions are dominant over the molecule-wall collisions.
- Viscous flow, where the mixture acts as a single fluid whose flow is promoted by the gradient of total pressure. In this case, the molecule-molecule collisions again dominate over the molecule-wall collisions.
- Surface diffusion is where the transport of the molecules over the surface in adsorbed state is dominant. This type of transport is usually negligible compared to the others, except for sufficiently small pore size, for which the adsorption forces are strong enough to constrain the molecule to mainly move over the surface. This kind of transport is usually precursors of phenomena like *multilayer adsorption* and *capillary condensation*.

The most important hypothesis that allows leading a usable mathematical form of the model is that all the involved transport modes act independently to each other. Under this hypothesis, the scheme behind the formalization of the Dusty-Gas Model can be represented by the following analog electric circuit (Fig. 1):



Dusty-Gas Model (DGM), Fig. 1 Analog electric circuit relative to the transport modes included in the Dusty-Gas Model

Neglecting surface diffusion and thermal diffusion, the mathematical form of the model can be expressed in the following manner:

$$\sum_{j=1}^n \frac{x_j \vec{N}_i - x_i \vec{N}_j}{C_T D_{ij}^{Bin} \frac{\varepsilon}{\tau}} + \frac{1}{D_i^{Kn} \frac{\varepsilon}{\tau}} \left[\frac{\vec{N}_i}{C_T} + \frac{x_i B_0 \frac{\varepsilon}{\tau}}{\eta} \left(\nabla P - C_T \sum_{j=1}^n x_j \vec{F}_j \right) \right] = -x_i \nabla \ln(x_i) - x_i \nabla \ln(P) + \frac{x_i \vec{F}_i}{RT} \quad (1)$$

where $\vec{N}_i$ [mol s⁻¹ m⁻²] is the total fluxes (i.e., diffusive + convective) of the *i*-th species, x_i its molar fraction, P [Pa] the total pressure, C_T [mol m⁻³] the total concentration, T [K] the temperature, D_{ij}^{Bin} [m² s⁻¹] is the binary diffusion coefficient relative to the generic species *i* and *j*, D_i^{Kn} [m² s⁻¹] is the Knudsen diffusivity, B_0 [m²] is a geometrical parameter depending on the structure geometry, η [Pa s] is the mixture viscosity, $\vec{F}_i$ is the resultant of all the possible external forces acting on the *i*-th species, and ε and τ are the medium porosity and tortuosity, respectively (all the vectorial entities are denoted with an arrow above).

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Dynamic Free Volume

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Dynamic free volume appears in liquids (Frenkel 1946) and in polymers above their glass transition temperatures T_g , i.e., in *rubbers*. In liquids, it appears due to mobility of individual molecules, while in *rubbers* due to segmental mobility. Dynamic free volume influences such properties of the medium as diffusion and self-diffusion coefficients and viscosity. In glassy state, where the segmental mobility is frozen, still some local mobility of small side groups is possible as well as the corresponding *free volume*. When a glassy polymer is plasticized, that is, contains low molecular mass additives, their mobility can induce some mobility of the adjacent parts of the main or side chains. So the fraction of dynamic free volume in the total *free volume* can increase, the polymer becomes more “rubberlike,” and its properties (gas permeation parameters) become more similar to those of rubbers: increase in permeability and decrease in permselectivity. These phenomena are detrimental for separation of gas mixtures that contain great concentration of highly sorbed components like carbon dioxide (Sanders 1988). According to *molecular dynamics*, the average time of “settled” life of free volume elements in rubbers is very short – about several picoseconds (Hofmann et al. 2000). The mobility of any kinetic system is determined by the relaxation time τ : $\tau(T) = \tau_0 \exp(U/kT)$, where U is the activation energy and $\tau_0 = 10^{-12}$ s. It is often assumed that U increases at decreased temperatures and, hence, the relaxation times at the glass transition temperature $\tau(T_g)$ become longer than the intrinsic times of cooling of the high elastic system, i.e., vitrification occurs. These changes of U are caused by the decreases in the dynamic free volume in rubbers v_f . The dynamic (or fluctuation) free volume above T_g increases

with temperature according to the equation: $v_f = v_{fg}[1 + (\alpha_r - \alpha_g)(T - T_g)]$, where α_r and α_g are the coefficients of thermal expansion above and below T_g , respectively, and v_{fg} is the free volume at T_g . Originally, it has been assumed that the fraction of free volume at T_g , $f_c = v_{fg}/v$, where v is the specific volume of the polymer, is constant for most of the polymers and equal 0.025 ± 0.003 (iso-free volume concept of Simha-Boyer). Further studies showed that f_c varied in a much wider range and increases with T_g (Yampolskii et al. 2000).

The variation of the dynamic free volume in rubbers with temperature and as a function of T_g has important implications for membrane science: when the difference $T_{exp} - T_g$ increases (at constant T_{exp}), i.e., for the rubbers with lower T_g , e.g., polydimethylsiloxane, the transport parameters such as $P(T_{exp})$ and $D(T_{exp})$ strongly increase (van Amerongen 1964; Yampolskii et al. 1982). Here, T_{exp} is the ambient temperature at which the permeability and diffusion coefficients are usually measured. It means that the polymers with the lowest glass transition temperature have the greatest dynamic free volume at ambient temperatures.

The size of the elements of dynamic free volume in rubbers is relatively large: it should be compared with the size of kinetic segments, so much larger than the size of the typical gaseous penetrants. It means that the selectivity of diffusion in rubbers is very weak, and, because of this, in rubbers *solubility-controlled permeation* regime is realized.

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Dynamic Mechanical Analysis

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Dynamic mechanical analysis (DMA) is a technique to study viscoelastic properties and modulus of elasticity of polymers by measuring the damping of an oscillatory signal of stress and strain. DMA results generally describe the variation of modulus values as a function of temperature or frequency (e.g., Fig. 1) and are widely used to detect the transitions such as glass transition temperature (T_g) or melting of polymer materials.

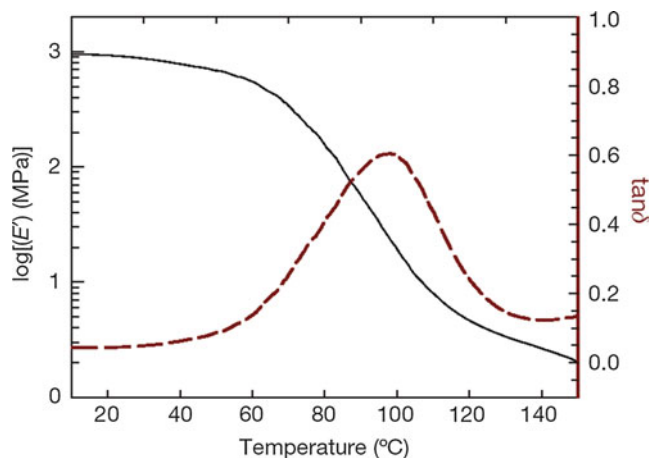
Figure 2a shows general schematic diagram of DMA apparatus; after a sinusoidal force is applied to the sample as an input signal, the resulting sinusoidal deflection or deformation is detected as an output signal, which contains information about the storage modulus E' , the dynamic loss modulus E'' , and the mechanical loss factor $\tan \delta$ (www.ngb.netzsch.com). According to the feature or types of sample materials, there are various modes of deformation as shown in Fig. 2b (www.ngb.netzsch.com), and this variety of sample holding method enables DMA to have wide

applications. For membrane samples, tension mode (fifth mode from the top in Fig. 2b) is generally adopted.

In the membrane applications, DMA is widely used for various fields such as fuel cell membranes, bio membranes, gas separation, pervaporation, etc. Page et al. applied DMA to investigate the structural characteristic of Nafion membranes well known as a fuel cell membrane (Page et al. 2005). In the study, two thermally reversible transitions of Nafion over room temperature were explained as glass transition by the short-range segmental motions within a static electrostatic network below 150 °C and the long-range chain/side-chain motion by thermally activated destabilization of the electrostatic network over 240 °C. Also, Xie reported that the perfluorosulfonic acid (PFSA) ionomer membrane showed a wide range of glass transition from ~55 °C to ~130 °C (Fig. 1), and based on the T_g result, he studied the multi-shape memory effect of PFSA (Xie 2010). Mano focused on the advantage of DMA that the test conditions can be more closely set to the physiological environments which the biomaterials will be applied to (Mano 2008). Using chitosan membranes, their mechanical properties were measured under low/moderate hydration conditions at different relative humidity (RH) levels and in completely wet (immersed) condition. Weng et al. synthesized intrinsically dopable polyimide (DPI) membranes containing an amine-capped

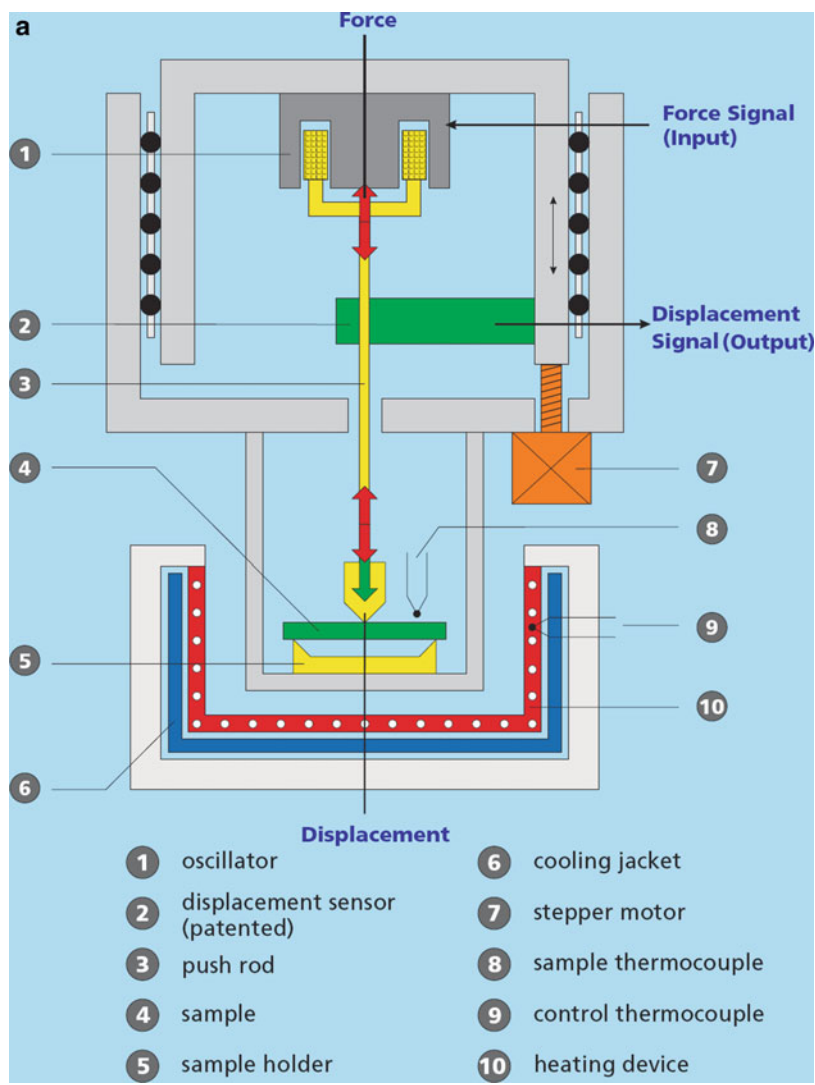
Dynamic Mechanical

Analysis, Fig. 1 Dynamic mechanical analysis (DMA) curve of perfluorosulfonic acid (PFSA) ionomer. $\tan \delta$ is the ratio between the loss modulus E'' and the storage modulus E' (Xie 2010) (Reprinted with permission from Macmillan Publishers Ltd: Nature 464:267–270, copyright (2010))

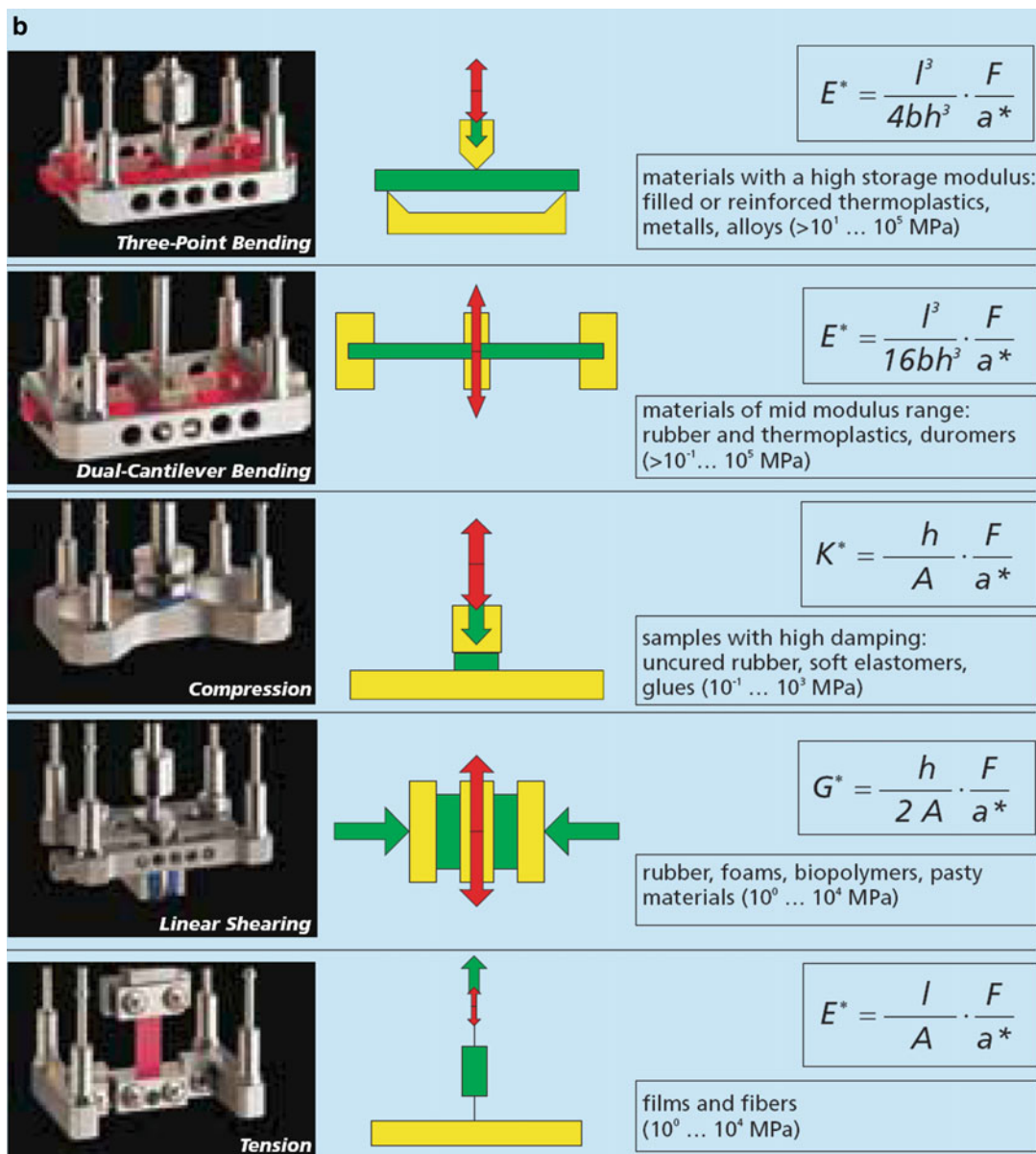


aniline trimer (ACAT) having high gas separation properties, where DMA results reported higher mechanical and thermal stabilities of the membranes than those of polyaniline (PANI) and conventional nondopable polyimide (NDPI) (Weng et al. 2011). Other examples are as follows: Budd et al. studied the mechanical stability of polymer of intrinsic microporosity (PIM-1) by DMA in the temperature range from 30 °C to 450 °C for pervaporation application (Budd et al. 2004); Nagarale et al. synthesized poly (vinyl alcohol)-SiO₂ hybrid membrane by

sol-gel method for a cation-exchange membrane, and its mechanical stability was measured by DMA (Nagarale et al. 2004); Gholap et al. synthesized hydrophobically modified PVA-g-polyNTBA membranes, where DMA was used to detect the crystallinity of the membranes as a function of annealing (Gholap et al. 2004); using DMA, Arjun and Ramesh studied the mechanical stability of the oxidatively stable polycarbonate urethane (PCU) membranes fabricated by electrospinning method for biomedical application (Arjun and Ramesh 2012); Ghassemi



Dynamic Mechanical Analysis, Fig. 2 (continued)



Dynamic Mechanical Analysis, Fig. 2 (a) General schematic diagram of dynamic mechanical analysis (DMA) apparatus and (b) modes of deformation (i.e.,

sample holding method) (www.ngb.netzsch.com) (Reprinted with permission from NETZSCH-Gerätebau GmbH)

et al. synthesized poly(arylene ether)s with pendant perfluoroalkyl sulfonic acid groups for fuel cell application, where their α -relaxation temperature was reported around 196 °C (Ghassemi et al. 2011); Love investigated thermal and mechanical transitions for commercially available polymer Li-ion battery separators (Love 2011).

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Dynamic Membrane Emulsification

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Dynamic membrane emulsification (ME) refers to the formation of emulsion droplets by extruding the to-be-dispersed phase through the membrane

pores into the continuous phase, and the droplet detachment occurs by a surface shear. The regular droplet detachment from the pore openings is obtained by:

- (i) Moving the continuous phase in cross-flow, stirred, or pulsed mode
- (ii) Moving the membranes by rotation, vibration, or oscillation

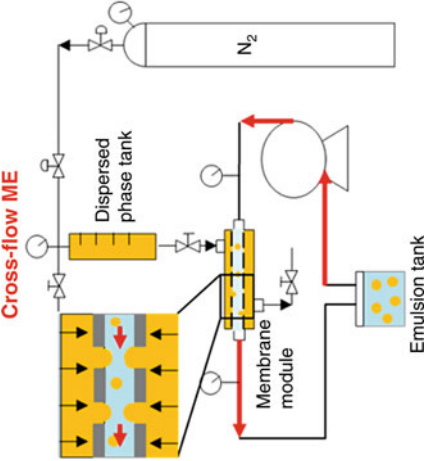
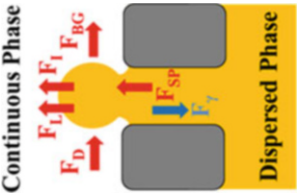
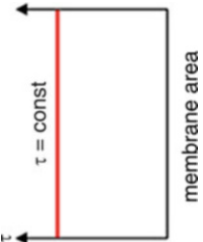
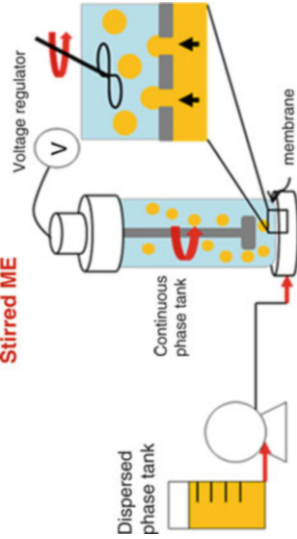
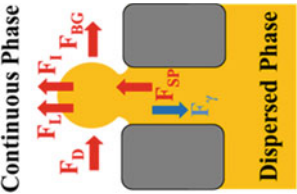
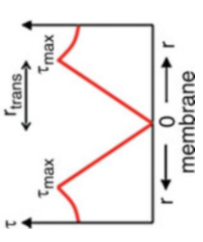
In Table 1, techniques, shear stress profile, and forces acting on a forming droplet for each membrane emulsification process are illustrated.

In cross-flow mode, the shear stress is generated by the recirculation of the continuous phase tangentially to the membrane surface. This technique is called “*cross-flow ME*.” A typical cross-flow ME apparatus includes a tubular or flat-sheet microfiltration membrane, a pump for the recirculation of the continuous phase along the lumen side of the membrane, a feed vessel, and a pressured nitrogen gas container for the dispersed phase (Peng and Fellow 1998). Cross-flow ME is suitable for large-scale production and continuous or semicontinuous operation. However, droplet breakup can occur over time when concentrated emulsion is produced due to the high cross-flow velocities used to obtain narrow droplet size distribution at high dispersed phase flux or over long time of operation.

In pulsed-flow mode, a periodic flow pulsation is generated in the continuous phase without recirculation. This technique is called “*pulsed-flow ME*.” In a typical pulsed-flow ME apparatus, the dispersed and the continuous phases are injected using a pump, while the pulsed flow in the continuous phase is generated by a frequency generator (Holdich et al. 2013) or by inverting the flow direction back and forward within the membrane lumen (Piacentini et al. 2014). Pulsed-flow ME is advantageous for the production of emulsions with a high dispersed to continuous phase ratio, and it is suitable for large-scale production in continuous or semicontinuous mode.

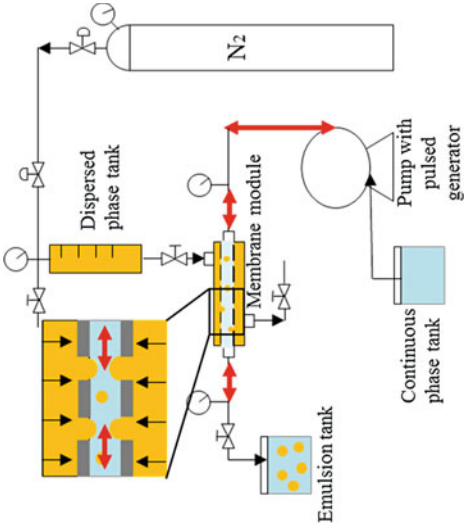
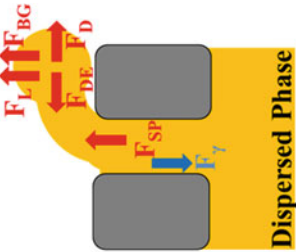
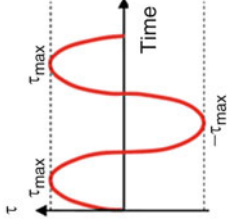
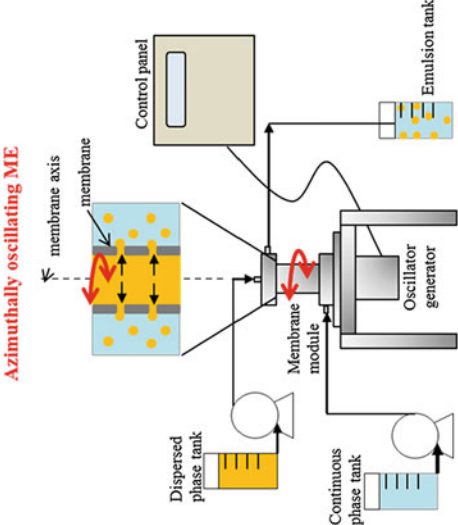
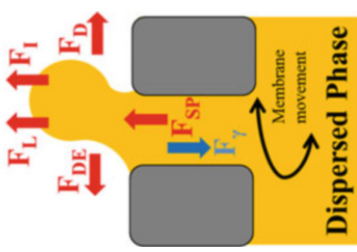
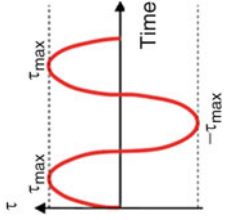
In an alternative, the shear stress on the membrane surface can be generated by stirring the continuous phase. This technique is called “*stirred membrane emulsification*.” In a typical stirred ME

Dynamic Membrane Emulsification, Table 1 Membrane emulsification techniques, shear stress profile, and forces acting on a forming droplet

ME plant	Forces acting on a drop at the pore level	Shear stress profile
Cross-flow ME 	Continuous Phase 	
Stirred ME 	Continuous Phase 	

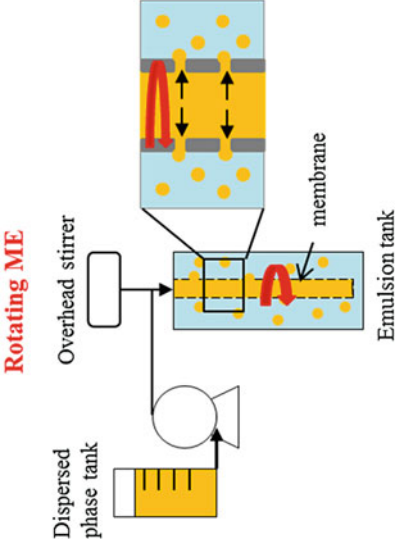
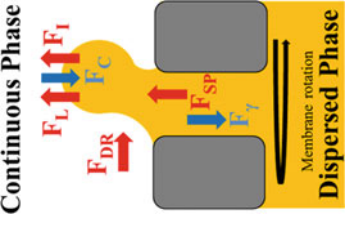
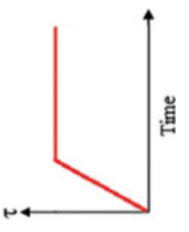
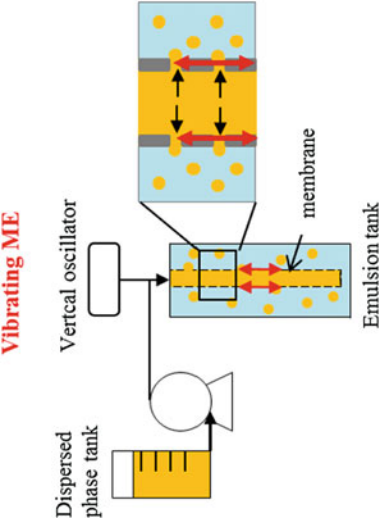
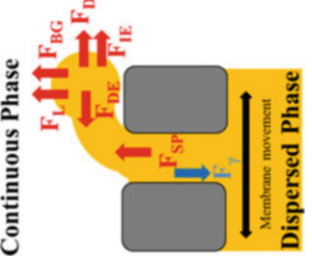
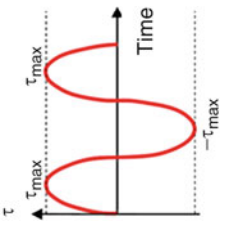
(continued)

Dynamic Membrane Emulsification, Table 1 (continued)

	Continuous Phase Continuous phase movement  Dispersed Phase	
Membrane emulsification based on moving the membrane ME plant <i>Azimutally oscillating ME</i> 	Continuous Phase Forces acting on a drop at the pore level  Dispersed Phase	

(continued)

Dynamic Membrane Emulsification, Table 1 (continued)

Rotating ME 	Continuous Phase 	
Vibrating ME 	Continuous Phase 	

device, the dispersed phase is injected through the membrane pores by using a pump or nitrogen gas while stirring the continuous phase with a rotator when a tube-shaped submerged membrane is used or with a paddle blade stirrer in the case of a flat-sheet membrane (Stillwell et al. 2007). Stirred ME is useful for emulsion production at batch scale, in the laboratory, and it is especially used to study the effect of different experimental conditions and chemistry on the formulation properties.

In *rotating ME*, the dispersed phase is introduced into the center of a rotating tubular porous membrane, and droplets are detached at the membrane wall in the radial direction into the stationary continuous phase (Vladisavljević and Williams 2006). The pressure is generated in the membrane lumen by using nitrogen gas or a pump, while the membrane is rotated in the continuous phase by an overhead stirrer. Rotating ME is particularly advantageous for the production of coarse emulsions and fragile structured products in which the droplets and/or particles are subject to breakage during the pump recirculation. However, the use for large-scale production is limited due to the complicated and more expensive design and higher power consumption compared to alternative designs.

The *vibrating ME* principle is similar to the rotating ME except for the use of oscillation of the membrane perpendicularly with respect to the dispersed phase injection direction (Holdich et al. 2010). The frequency and amplitude of the axial oscillation of the membrane was generated by an electrically driven vertical oscillator and could be controlled separately.

In *azimuthally oscillating ME*, a tubular membrane is periodically rotated back and forward in a slowly cross-flowing continuous phase, while the dispersed phase is radially injected in the lumen side of the membrane using a pump (Silva et al. 2015). The azimuthal (tangential) oscillation of the membrane is controlled by a control panel which is connected to the oscillator motor providing separate control over the frequency and membrane displacement. Azimuthally oscillating ME operates in a continuous mode, and it is suitable for large-scale production providing high

production rates, facilitating easy process automation and reduced operation time.

In dynamic ME, the forces acting on a droplet at the membrane pore level include detaching forces, driving droplets off the pore, and retaining forces, holding droplets on the pore. Detaching forces are drag (F_D), buoyancy (F_{BG}), inertial (F_I), lift (F_L), and static pressure (F_{SP}) force, while the main retaining force is the interfacial tension (F_γ). The drag force (F_D) is created either by moving the continuous phase parallel to the membrane surface or by moving the membrane; the buoyancy force (F_{BG}) is due to the density difference between the continuous phase and the dispersed phase; the inertial force (F_I) is caused by the dispersed phase flow moving out from the pore outlet; the dynamic lift force (F_L) results from the asymmetric velocity profile of the continuous phase near the droplet; static pressure (F_{SP}) force is due to the pressure difference between the dispersed phase and the continuous phase at the membrane surface; the interfacial tension force (F_γ) represents the effect of dispersed phase adhesion around the edge of the pore opening. In the case of “moving membrane” emulsification, additional (or enhanced) forces have to be considered.

For rotating membrane emulsification, compared to a nonrotating system, the drag force created by the membrane rotation (F_{DR}) has to be taken into account, and the gravitational body force is replaced by the centrifugal force (F_C) resulting from centrifugal acceleration and density difference of the two phases. High centrifugal force may be responsible for polydisperse emulsion production in the case of O/W emulsion due to deformation of the emerging oil drops and induced flow of oil drops toward the membrane surface causing coalescence and wetting of the membrane.

For an oscillating membrane system where the membrane is axially excited, an additional drag force (F_{DE}) and inertial force (F_{IE}) appear in the direction parallel to the membrane. This is due to a sudden change in the direction of the membrane which induces a velocity difference in the column of liquid inside the membrane and localized high pressure at the peak positions of the vertical oscillation (i.e., top and bottom of the membrane tube).

In *dynamic* ME, the droplet breakup process is correlated with a *dripping* or *jetting* behavior depending on the relative strength of the different forces acting on the process. In the dripping region, the inertial force is negligible compared to the drag force or unable to overcome the surface tension force. Thus, the droplet size is affected mainly by the drag force imparted by the continuous phase flow or moving membrane and the surface tension force. The inertial force of the dispersed phase has negligible effect in drop detachment in the dripping mode. It is shown that the droplet size becomes smaller as the shear stress increases and the influence is more significant for low shear values and smaller pore size. At high dispersed phase flow rates, the inertial force exceeds the surface tension force, leading to a transition to jetting behavior. In this case, the droplet detachment point moves further downstream from the pore usually resulting in the formation of a larger droplet than when in the dripping regime.

The different process conditions can be accurately tuned to control the shear stress in dynamic ME according to the mechanism used to generate the drag force (flowing of continuous phase or moving membrane); the following provides some simplified equations for shear at the membrane surface according to the method of generation of that shear:

- In cross-flow ME, the shear stress (τ) [Pa] is constant over the tubular membrane area, and it is correlated with the tangential velocity of the flowing continuous phase (v) [ms^{-1}], the density of the emulsion (ρ) [kgm^{-3}], and the friction factor (λ) which is calculated depending on the Reynolds number ($\lambda = 16/\text{Re}$ for $\text{Re} < 2000$; $\lambda = 0.0792 \text{ Re}^{-0.25}$ for $\text{Re} > 2000$) Eq. 1:

$$\tau = \frac{\lambda \rho v^2}{2} \quad (1)$$

- In stirred ME, the shear stress (τ) [Pa] depends on the angular velocity (ω) [s^{-1}] of the stirrer. The shear over the whole membrane area can be calculated with the Eqs. 2 and 3:

$$\tau_{\max} = 0.825 \mu_c \omega r_{\text{trans}} \frac{1}{\delta} \quad \text{for } r < r_{\text{trans}} \quad (2)$$

$$\tau = 0.825 \eta_c \omega r_{\text{trans}} \left(\frac{r_{\text{trans}}}{r} \right)^{0.6} \frac{1}{\delta} \quad \text{for } r < r_{\text{trans}} \quad (3)$$

where μ_c [Pa s] is the continuous phase viscosity, r_{trans} is the transitional radius, and δ is the boundary layer thickness given from the Landau-Lifshitz equation ($\delta = \sqrt{\mu/\omega\rho}$). The shear stress is not uniformly distributed over the membrane surface, and it can be assumed that the maximal shear ($\tau_{\max}$) is reached at distance r_{trans} from the center of the membrane; r_{trans} is the transitional radius in which the rotation changed from a free vortex to a forced vortex.

- In rotating ME, the shear stress is directly proportional to the membrane rotational speed (n) [rpm] but depends also on the width of the annular gap between the rotating membrane and the stationary vessel. The shear at the surface of the membrane is calculated using Eq. 4:

$$I? = \frac{I?R_1^2 n}{15(R_2^2 - R_1^2)} \quad (4)$$

where R_1 is the radius of the rotating membrane and R_2 is the radius of the stationary vessel.

- Pulsed ME and vibrating and azimuthally oscillating ME are based on the generation of the shear stress by oscillation of either the continuous phase or the membrane. Thus, there are two parameters affecting shear stress on the membrane surface: frequency (f) [Hz] and amplitude (a) [m] of the oscillation. During the oscillation, the shear is variable and the emerging drop detaches when it experiences the maximum shear stress which is calculated using Eq. 5:

$$\tau_{\max} = 2a(\pi f)^{3/2}(\mu\rho)^{1/2} \quad (5)$$

where μ is the viscosity and ρ is the density of the continuous phase. A peak shear event occurs twice per oscillation: once in each direction that the wave

is moving, for a regular wave form such as a sine wave.

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Dynamic Membrane Microfiltration

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Introduction

To separate molecules or particles from a solution by cross-flow filtration through a membrane, it is necessary to circulate the fluid at a speed of $3\text{--}6\text{ ms}^{-1}$ in a tubular or plane membrane in

order to prevent the buildup of a layer of rejected solutes on the membrane while exerting a pressure on the fluid to produce a filtrate. The combination of high feed pressure and flow rate requires powerful and expensive pumps that consume energy and the friction creates a pressure decay along the membrane which reduces the transmembrane pressure (TMP). In addition, the rejected molecules or particles can create a cake on a microfiltration (MF) membrane which reduces both filtration rate and solute transmission through the membrane.

Dynamic filtration is a recent alternative to classical cross-flow filtration (Lee et al. 1995; Jaffrin 2008) consisting in creating a high shear rate (velocity gradient) at the membrane by a disk or a rotor rotating near the membrane or by using rotating or vibrating membranes, while using a low feed flow rate, only slightly larger than the permeate flow rate.

Advantages and Drawbacks of Dynamic Filtration

The first advantage is a substantial increase in permeate flux at all membranes cut-off due to shear rates which can reach $3\text{ }10^5\text{ s}^{-1}$ when using disks with radial vanes rotating at high speed. Due to moderate fluid velocities inside the module, the transmembrane pressure remains relatively uniform, which contributes to flux increase. Clarification of a suspension by MF requires a good solute transmission which is augmented by cake reduction. In ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) the permeate flux is mainly limited by the concentration polarization layer made of molecules rejected by the membrane. This layer is diminished by high shear rates which increases back transport of solutes away from the membrane. The flux keeps increasing with rising TMP until pressures of 40 bars at high shear rates. The combination of these two factors, high TMP and high shear rates, yields frequently permeate fluxes five times higher than in cross-flow filtration with the same membrane and same fluid. In addition, in NF and

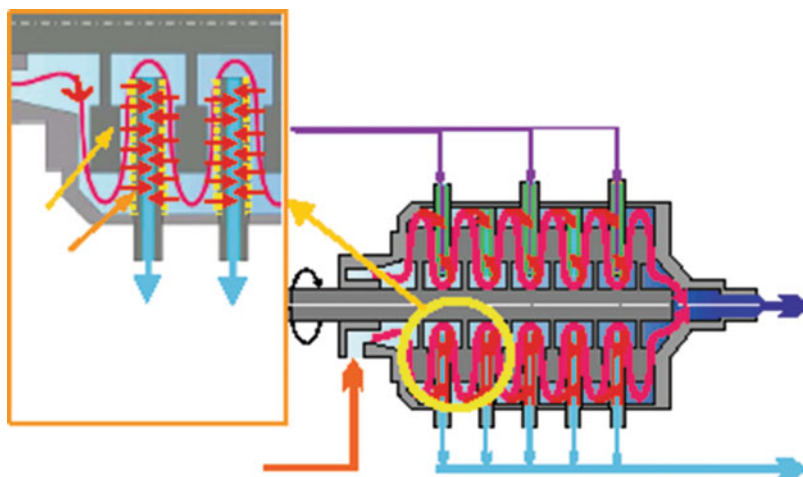
Dynamic Membrane Microfiltration,

Fig. 1 Industrial VSEP vibrating modules (Courtesy of New Logic Research)



Dynamic Membrane Microfiltration,

Fig. 2 Dyno rotating disk module (Bokela, Germany)



RO applications, such as wastewater treatment, it is important to have a small microsolutes concentration in permeate. This is the case in dynamic filtration as the diffusive mass transfer through the membrane is greatly reduced by the small solute concentration at the membrane.

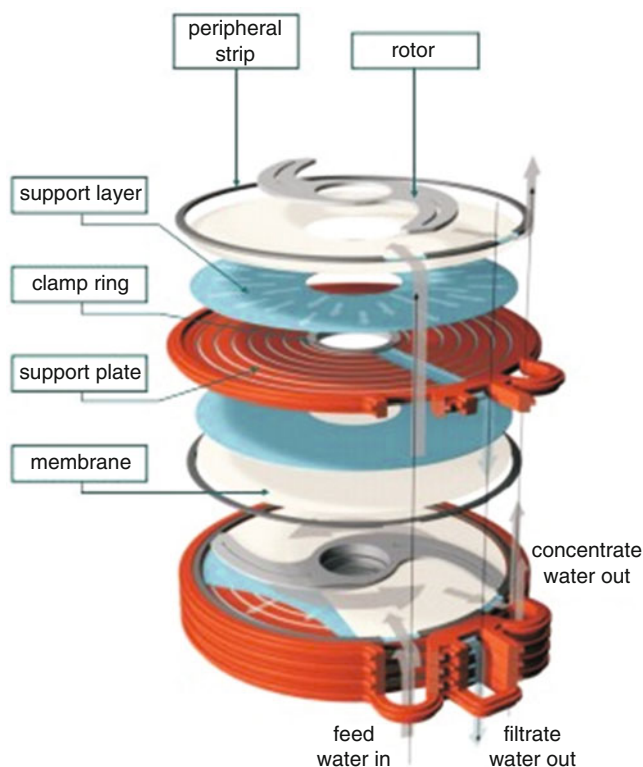
The main drawbacks are higher costs of equipment and maintenance due to moving parts and more complex design and membrane area limitations for some systems. The recent availability of 30 cm diameter ceramic membrane disks has permitted the development of systems with ceramic

disks rotating around several parallel shafts in a closed tank, with a total membrane area exceeding 120 m^2 which are cheaper to build and to service than multicompartiment modules with metal disks rotating between fixed organic membranes.

Rotating disks modules give a choice between using high rotation speeds to maximize the flux and thus minimize membrane area and investment cost, or to use moderate speeds to obtain the same flux as with tubular membranes but saving more than 60 % of the energy spent per m^3 of permeate with these membranes.

Dynamic Membrane Microfiltration,

Fig. 3 Sketch of OptiFilter CR, Metso paper Co, Finland



Dynamic Membrane Microfiltration, Table 1 List of industrial dynamic filtration modules and their characteristics (Jaffrin 2008)

Manufacturer	Models	Type	Membrane area m ²	Pore size	Disk diam, mm	MaxTMP bar
Bokela (Germany)	Dyno	Rotating disks	0.013–12 organic	10 nm–1 μm	137–850	4
Andritz (Germany)	Kraus-M DCF	Membrane rotating on two shafts	0.05–16.4 ceramic	7 nm–2 μm		2
Novoflow (Germany)	SSDF CRD	Membrane rotating on one shaft	1–25 ceramic	7 nm–2 μm	152–500	2,5
Metso paper (Finland)	Optifilter CR	Rotors between membranes	15-84-140 Organic	MF-UF	550–1000	3–4
Spintek (US)	ST	Membr rot on 1 shaft	0.1–2.3 Org/ceram	MF-UF	275	
New Logic Research, (US)	VSEP	0.05–150 organic	Organic	MF-UF-NF-RO	300–500	40

Industrial Filtration Modules

VSEP Vibrating Modules (New Logic Research, Ca, USA)

Close to 400 VSEP systems have been installed worldwide since their introduction around 1995.

They consist of a stack of circular organic membranes in separate compartments oscillating azimuthally around a vertical shaft at a resonant frequency of about 60 Hz. The maximum membrane area is 150 m² and the power spent in vibrations is only 9 kW (Fig 1). It can sustain

pressures of 40 bars and is used with a wide choice of membranes from MF to RO Al-Akoum et al. (2002).

Single Shaft Rotating Disks Systems

Bokela GmbH (Karlsruhe, Germany) commercializes the Dyno with metal disks rotating between fixed circular membranes of 12 m² for MF and UF (Fig. 2).

Metso Paper (Raisio, Finland) manufactures the Optifilter CR with blades rotating between fixed membranes of 1 m diameter and up to 140 m² membrane area with a 132 kW motor (Fig. 3).

Multishaft Rotating Ceramic Membrane systems

KMPT GmbH (Vierkirchen, Germany) commercializes a two-shaft module with 15 cm diameter overlapping ceramic membranes of 16.4 m² area (Table 1).

Conclusion

Dynamic filtration is not intended for initial treatment of huge volumes of fluids, but it should be well adapted to “end of pipe treatment” when the goal is to reach high solid concentration in retentate or to extract valuable components in highly charged suspensions.

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Dynamic Optimization of Membrane Operation

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Dynamic optimization is usually referred to open-loop optimal control. It encompasses several methods whose purpose is to determine trajectories of dynamic (time-dependent) variables in optimal manner. These methods may be used to find optimal control of processes or to design optimal experiments for parameter estimation. The generalized representation of dynamic optimization problem (DOP) is as follows

$$\min_{\mathbf{u}(t)} \mathcal{G}(\mathbf{x}(t_f), t_f) + \int_{t_0}^{t_f} \mathcal{F}(\mathbf{x}(t), \mathbf{u}(t), t) dt \quad (1)$$

$$\text{s.t. } \dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}(t), \mathbf{u}(t), t) \quad (2)$$

$$\mathbf{h}(\mathbf{x}(t_0), t_0, \mathbf{x}(t_0), t_f) = 0 \quad (3)$$

$$\mathbf{g}(\mathbf{x}(t), \mathbf{u}(t), t) \leq 0 \quad (4)$$

where t is time, $\mathbf{u}(t)$ denotes vector of control variables, $\mathbf{x}(t)$ is vector of state variables, and $G(\cdot)$ and $F(\cdot)$ stand, respectively, for nonintegral and integral part of optimization objective. The set of differential Eq. (2) represents dynamical system. This is usually the model of the process whose optimal control one searches for. Sets of functions $\mathbf{h}(\cdot)$ and $\mathbf{g}(\cdot)$ may express various types of equality/inequality constraints which are imposed by the physical reality.

In order to find solution to DOP, one can exploit various techniques, stochastic (such as genetic algorithms, simulated annealing, etc.) or deterministic ones. Deterministic methods are based on the following three principles: variational calculus (developed by Euler and Lagrange), dynamic programming (Bellman 1957), and Pontryagin's maximum/minimum

principle (Pontryagin et al. 1962). The latest one gave rise to most popular numerical techniques such as control vector parameterization, control vector iteration, boundary condition iteration, orthogonal collocation, and multiple shooting techniques.

Various dynamic optimization problems were solved already in literature on membrane processes. These applications include optimization of membrane reactors performance (Parvasi et al. 2009; Rahimpour and Elekaei Behjati 2009), other membrane-assisted processes (Kuhn et al. 2009; Bui et al. 2010), membrane separation (Fikar et al. 2010; Paulen et al. 2011) as well as membrane fouling and cleaning (Van Boxtel and Otten 1993; Blankert et al. 2006; Zondervan and Roffel 2008).

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Dynamic-Volume Diafiltration

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Dynamic-volume diafiltration is a type of batch diafiltration process that is designed to achieve the twin aims of simultaneous macrosolute concentration and microsolute removal by employing optimal time-varying control of diluant feeding.

The technological goal in a general batch process is to increase the macrosolute concentration from $c_{1,0}$ to $c_{1,f}$ and to reduce the microsolute concentration from $c_{2,0}$ to $c_{2,f}$. The fractionation is accomplished by introducing a diluant into the feed reservoir. Choosing the right strategy of scheduling the addition of diluant is a critical aspect to consider in batch processing (Lutz 1997). Processes can be characterized upon their α -strategies (α is the ratio of diluant flow rate to permeate flow rate). Frequently used batch diafiltration techniques, such as traditional diafiltration, variable-volume diafiltration, pre-concentration followed by variable-volume diafiltration, intermittent feed diafiltration, and sequential dilution diafiltration, employ arbitrarily predefined schemes of diluant addition. In contrast, dynamic-volume diafiltration is designed by the evaluation of the optimal time-

varying profile of diluant flow for the entire course of operation.

The process of dynamic-volume diafiltration poses a dynamic optimization problem (Fikar et al. 2010). The goal of optimization is to find the optimal time-dependent function of α that drives the process from its initial state to a prescribed terminal state. Optimality is defined as the minimization of the objective function J without violating given constraints. The mathematical problem can be formulated as follows:

$$\begin{aligned} \min_{\alpha(t)} \mathcal{J} \quad & \text{s.t.} \\ \dot{c}_1 &= \frac{c_1 q}{V} (R_1 - \alpha), \quad c_1(0) = c_{1,0}, \\ c_1(t_f) &= c_{1,f}, \quad \dot{c}_2 = \frac{c_2 q}{V} (R_2 - \alpha), \\ c_2(0) &= c_{2,0}, \quad c_2(t_f) = c_{2,f}, \\ \dot{V} &= (\alpha - 1)q, \quad V(0) = V_0, \\ \alpha &\in [0, \alpha_{\max}] \end{aligned}$$

where c_1 , c_2 , and V represent the actual macrosolute concentration, microsolite concentration, and volume in the feed tank, respectively. It is assumed that the system is well mixed and the diluant is solute-free. R_1 and R_2 denote the rejection of macrosolute and microsolite, respectively. It should be mentioned that, in a general case, the actual value of both q and R depends on the concentrations of macrosolute as well as on microsolite. Moreover, process parameters (e.g., pressure, temperature, hydrodynamic conditions, etc.) also affect q and R .

In practice, several objective functions can be considered for optimization, for instance, time minimization:

$$J_A = t_f$$

diluant minimization:

$$J_B = \int_0^{t_f} \alpha(t) q(t) dt$$

or minimization of complex economic index:

$$\begin{aligned} J_C = & k_1 t_f + k_2 \int_0^{t_f} c_1 [1 - \mathcal{R}_1(t)] q(t) dt \\ & + k_3 \int_0^{t_f} \alpha(t) q(t) dt \end{aligned}$$

where total cost is a sum of three terms that are the operational cost of the pump, cost of the valuable component loss, and the cost of the utilized dilution water. k_1 , k_2 , and k_3 , are the respective cost factors.

This technique can be useful to evaluate optimal operation of membrane filtration plants including reverse osmosis, ultrafiltration, nanofiltration, and microfiltration systems (Paulen et al. 2012). In general, optimal α control need not to be any of the conventional diafiltration concepts, and thus, it might need advanced control systems. In many cases, however, it might be attractive to implement the optimal trajectory since it can lead to reduced operation time, diluant consumption, and product losses. The computed optimal profile may vary case by case depending on the complexity of the membrane response model, the initial and final values, and the constraints involved in the model.

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Ease of Expansion in Gas Separation

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Quite often during the operation of a system for the treatment of gases, it is necessary to expand it for treating greater streams. In some cases, future expansion is contemplated even during the initial phase of a project. In other cases, it could be a necessity not foreseen during system design phase (Miller and Stöcker 1989; Brunetti et al. 2010).

Membrane system expansion is very easy, since this only requires the addition of identical modules. This is the advantage offered by the modularity of membrane units and the reduced equipment and control systems required for operating it. In comparison, considering the other reference technologies for gas separation, PSA and absorption systems can also be expanded, but it requires additional design considerations and adds cost in the initial phase of the project.

The cryogenic units cannot be expanded if it is not foreseen during the design phase. Generally they can be over-dimensioned, and a capacity increase is often obtained without modification to the cold box itself through addition of a tail gas compressor.

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Effective Diffusivity

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Effective diffusivity is a convenient parameter which is introduced when diffusion takes place in non-homogenous media. Consider, for example, the case where a species is diffusing through porous particles, such as reactant diffusing inside a catalytic solid. In this case, the molecules have to travel for a longer distance given that the pores of the catalytic particles are not straight, and moreover diffusion takes place over a smaller area due to the solid being wall impermeable. These effects are taken into account by defining an effective diffusivity as

$$D_{eff} = D \left(\frac{\varepsilon}{\tau} \right)$$

where ε is the particle void fraction and thereby takes into account the reduced flow area available and τ is the tortuosity which considers the longer distance traveled by the molecules. It should be stressed, however, that more often than not, the parameter inside the parenthesis is utilized as a fitting factor derived from experimental data rather than predicting factor from the solid physical characteristics. These result in the reported tortuosity factor, for example, to assume rather wild values, as high as ten, which are difficult to justify with geometrical arguments alone.

The concept of effective diffusivity is also applied for the case of species diffusing in heterogeneous media, such a polymer filled with a second, less permeable, material. Maxwell (1873) has obtained an exact expression, in the case of composite media filled with spheres, for the effective diffusivity given as

$$D_{eff} = D \frac{\frac{2}{D_s} + \frac{1}{D} - 2\phi \left(\frac{1}{D_s} - \frac{1}{D} \right)}{\frac{2}{D_s} + \frac{1}{D} + \phi \left(\frac{1}{D_s} - \frac{1}{D} \right)}$$

where D is the diffusion coefficient in the primary media, D_s the diffusion coefficient through the spheres, and ϕ the sphere volume fraction. For the limiting case of the spheres being completely impermeable, Maxwell expression simplify to

$$D_{eff} = D \frac{1 - \phi}{1 + \frac{\phi}{2}}$$

Various empirical expressions have been reported in literature in order to take into account the deviation from sphericity of the foreign material. Particularly simple and efficient is the expression proposed by Nielsen (1967):

$$D_{eff} = D \frac{1 - \phi}{1 + \frac{\alpha\phi}{2}}$$

where α is the dispersed material aspect ratio. Nielsen relationship has been shown to do a satisfactory job against experimental evidence (Di Felice et al. 2008).

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Effectiveness Factor

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The concept of effectiveness factor is utilized when the effect of diffusion on the overall rate of a reacting process wants to be taken into account. Let's consider a catalytic solid particle where a reaction takes place. For a species to react, it must, at the same time, diffuse inside the catalytic particle and react. It is intuitive that the diffusion step slows the overall process rate, and an effectiveness factor is defined as

$$\eta = \frac{\text{actual rate of process}}{\text{rate of process if diffusion were infinitely fast}}$$

This definition is equivalent to consider reactant concentration on any point in the catalytic particle equal to that at the external surface.

A rather straightforward mass balance allows the determination of the effectiveness factor for a single cylindrical pore where a first-order reaction is taking place on the wall:

$$\eta = \frac{\tanh\phi}{\phi}$$

where ϕ is the Thiele module defined as

$$\phi = L \sqrt{\frac{k}{D_{eff}}}$$

with L the pore length, k the chemical reaction kinetic factor, and D_{eff} the reacting species effective diffusivity.

As expected the effectiveness factor approaches 1 when Thiele module is very small, i.e., for very short pores or very slow reaction or very high diffusion coefficients. On the other hand, for very high value of Thiele modules, effectiveness factor approaches the inverse of the Thiele module.

The above result can be easily generalized for the case of flat plate by putting L equal to half the plate width, for the case of long cylindrical pellets by putting L equal to half the pellet radius, and to the case of spherical pellets by putting L equal to one third the sphere radius. Extension to kinetic different from the first order has been presented in literature, and a summary can be found, for example, in Satterfield (1991).

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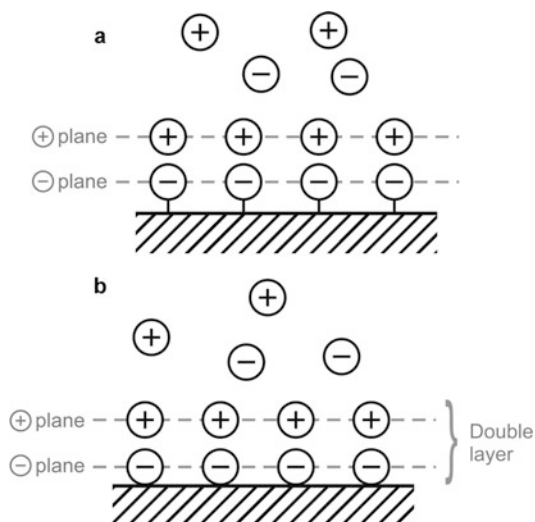
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Electrical Double Layer

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An electrical double layer is usually considered to form at the phase interface between two electrically conducting media. In such a case, on one side of the interface, an excess of positive charge exists, which is counterbalanced by an identical excess of negative charge localized on the opposite side of the interface. The overall system charge is thus equal to zero. In membrane science, this definition has, to a certain degree, been modified, the reason being that membranes can be produced from a broad spectrum of materials, including (i) electronic conductors (e.g., metals), (ii) ionic conductors (e.g., O^{2-} -conducting ceramics), (iii) functionalized polymers providing ionic conductivity through the liquid filling the



Electrical Double Layer, Fig. 1 Schematic sketch of structure of the Electrical Double Layer for (a) functionalized and (b) nonfunctionalized membrane materials

void volume of the material (ion-selective membranes), and (iv) nonfunctionalized polymeric or ceramic membranes.

Whereas, in the first two cases, the traditional definition is valid, in the last two, the situation is different. This is due to the fact that the bulk membrane material is neither an electronic nor an ionic conductor. Hence the double layer only forms on one side of the phase interface. The Fig. 1 provides a schematic sketch of the two mentioned cases. In the case of functionalized materials, the charge-carrying groups covalently bound to the polymeric backbone are oriented towards the void volume of the membrane interior, thus forming an electrically charged film covering the phase interface on the side of the solution. The charge of this film is compensated by that of the mobile ions present in the solution and located close to the film (see Fig. 1a).

In the case of the non-functionalized materials, the surface charge fixed to the surface of the solid phase is formed by specific adsorption of ions of one sign. Both the sign of the adsorbed ions and the extent of the adsorption are determined by the properties of the membrane material. In this case, too, the fixed charge is compensated by the charge

of ions moving in the system and located close to the absorbed surface film (see Fig. 1b).

An electrical double layer significantly influences the properties of the membrane, mainly with respect to its transport properties and behavior under current load. In selected cases the surface of the membrane materials is modified to achieve the preferred adsorption and thus the required transport and properties, including selectivity.

Electrical Interactions in Membranes

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In general electrical (electrostatic) interactions arise as a result of the interaction of electrically charged particles (charge carriers) with surrounding matter (electrically charged and neutral) (Stuart 1989). In the case of membranes, probably the most important interactions to consider are those between electrically charged bodies, such as ions dissolved in solution and ion-conducting, functionalized, or even inert membranes. In living systems the electrostatic interactions between the charged/polar and neutral/nonpolar side of a solute molecules with each other and with a solvent are responsible for the formation/assembly of monolayer and bilayer biological membranes and their functioning.

On the fluid side the charge carriers are typically mobile ions or colloidal particles of organic and inorganic nature. These carriers interact with the charge carriers fixed in the material of the membrane (see also the electrical double layer). The charge fixed in the membrane material is, in principle, of dual origin: (i) it comes from the component introduced and incorporated during its synthesis, and (ii) it is the result of the specific adsorption of ions on the surface of the solid phase. Electrostatic interactions between fixed and freely moving charge carriers are responsible not only for several phenomena characteristic of

membrane separation processes, such as the existence of Donnan potential, the selectivity of mass transport, or mass transport enhancement under current load by electroosmotic flux, but also for the existence of life itself. These facts document the importance of electrical interactions in membrane materials with respect to their transport properties.

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Electrical Potential

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Electric potential is a scalar physical quantity determined by the electric energy (or work in general) necessary to transfer a unit positive electric charge from infinity to the point of interest in a studied system. The point in infinity is formally chosen as a reference state characterized by zero electric potential. From this more or less abstract and intuitive definition of the reference state, it is apparent that the absolute value of electric potential is not available experimentally. However, it is possible to measure electric potential difference, known as voltage.

We can distinguish between outer (external) and inner (internal) electric potential. In the case of outer electric potential, the charge is transferred to the closest proximity of the external surface of the phase *P*. However, the distance from this surface has to be large enough to avoid the appearance of molecular and image forces. At the same time it should not cause any weakening of the electric interaction with the charge located on the internal side of the phase interface. The inner

electric potential is determined by the strength of the electric field in the interior of the phase P . It thus represents the work necessary to transport the charge from infinity to the phase P . The difference between the inner electric potential and the outer electric potential corresponds to the surface potential of phase P (Arthur and Alice 1997).

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Electrical Work in Membranes

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An electrical work is defined as the work connected with the charge carrier transport between two points in an electric field, i.e., from point of potential φ_1 to point of potential φ_2 . Thus, electrical work in membranes is the product of the transported electrical charge and the difference in electric potentials between which it has passed (Arthur and Alice 1997). Since the resistivity of the membrane can be approximated by ohmic resistivity, the electrical work dissipated in the membrane is equal to the ohmic potential loss in the membrane multiplied by the current load. Expressed alternatively, it is equal to the square of the current load multiplied by the ohmic resistivity.

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Electrically Enhanced Processes by Membrane Operations

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Electrically membrane operations are typically limited to systems involving electrically charged particles. In such a case, the application of an electric field can often significantly enhance the ongoing process. In selected cases, it is the application of an external electric field that makes the desired processes possible at all. By applying an electric field, electrically charged particles are dragged in the direction determined by the polarity of their charge and the vector of the electric field. This movement is responsible for electric current flow through the system. Part of the electric charge carried by one type of particles corresponds to what is known as the transference number of the given particle. It is proportional to the particle mobility in the system and the electric charge it carries (Colin 1976).

In the case of membrane operations enhanced by an electric field, generally functionalized ion-selective membranes are considered. Electrodialysis and dialysis are typical representatives of an electrically enhanced and a nonenhanced process, respectively. Electrodialysis is used to desalinate a treated stream containing dissolved ions by transporting them, due to the action of the electric field, against the concentration gradient to the concentrate stream (Fernando et al. 2011). In the case of dialysis the situation is the reverse, since the dissolved species move in the direction of the concentration gradient away from the treated stream to the solution free of the removed components flowing along the opposite side of the membrane. It is thus clear that electrodialysis is typically a significantly more intensive process in terms of the desalination rate. At the same time, it produces a significantly lower volume of the stream carrying the removed components. The electric field thus enhances the intensity of the

mass flux during membrane processes involving charged species and makes it possible to transport the charged species against the concentration gradient. On the other hand, dialysis is not limited to charged particles.

Electrically enhanced membrane operations can also be carried out with nonfunctionalized membrane materials or with membrane materials carrying no fixed electric charge, electrofiltration being an example. Here, the applied electric field influences the membrane operation indirectly by preventing blockage of the membrane surface. This is ensured by the electrophoretic transport of the charged colloidal particles concentrated in the solution away from the surface of the filtering membrane, see also Electrofiltration.

It is, therefore, evident that the application of an external electrical field can significantly enhance or modify processes, including membrane operations.

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Electrochemical Deposition

- [Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices](#)

Electrochemical Impedance Spectroscopy

- [Impedance Spectroscopy, Membrane Characterization by](#)

Electrochemical Impedance Spectroscopy (EIS)

- [Impedance Spectroscopy](#)

Electrochemical Membrane Bioreactor

- [Bioelectrochemical MBR](#)

Electrochemical Processing

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In electrochemical processing, electrical energy is supplied to or obtained from the electrochemical system in order for chemical production or energy conversion to take place (Bard and Stratmann 2007). The first group of processes, also called electrolytic, is not spontaneous. The second group of processes, called galvanic, is spontaneous and it delivers electrical energy. Electrolytic processes can be further divided into two categories: inorganic and organic. In inorganic electrochemical processing, important commodity chemicals such as sodium hydroxide, chlorine, and pure metals are produced. The major inorganic electrochemical processing technologies are chlor-alkali electrolysis and electrowinning of metals like aluminum or copper. Nowadays, hydrogen production by water electrolysis gets more on importance in context of chemical storage of renewable electrical energy (wind and photovoltaic) in hydrogen. The most significant commercial electroorganic synthesis is Monsanto's electrohydrodimerization (EHD) of acrylonitrile to adiponitrile. Adiponitrile has an importance in production of nylon 6-6. Examples of galvanic systems are fuel cells and batteries. The main "product" of galvanic systems is electrical energy.

Electrochemical systems have some intrinsic advantages over other types of chemical systems like better control of a reaction rate, operation at lower temperatures, and less environmental impact. They take place in an electrochemical reactor. The design of an electrochemical reactor is influenced by the state of aggregation of reactants (gas, liquid, or solid), necessity of reactants and/or products separation, required mass transport conditions, and electrode materials. If product or reactant separation is required, an electrochemical reactor must contain a separator, which is a membrane. Major requirements on a membrane are good separation efficiency, low electrical resistance, no electron conductivity, low cost, long operating life time, good dimensional stability, and resistance to plugging and fouling. In general permeable and semipermeable membranes have been applied in electrochemical processing. Permeable membranes are porous materials filled with liquid electrolyte which permit the bulk flow of liquid through their structure and are thus nonselective regarding transport of ions or neutral molecules. In electrochemical processes, these are also referred to as diaphragms. Permeable membranes can be made of inorganic and organic materials and composites. Examples of these materials are asbestos (chlor-alkali electrolysis), polymers like polyethylene and polypropylene (batteries), or composites like polymer (polypropylene)-modified asbestos. Semipermeable membranes permit the selective passage of certain species by virtue of molecular size or charge. In electrochemical processes, ion-conducting membranes (see solid electrolyte) are broadly applied. In general, ion-conducting membranes have higher separation efficiency and lower electrical resistance than diaphragms, but they are also more costly and impose higher requirements on system purity.

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Electrochemical Regeneration

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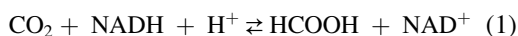
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In electrochemical regeneration electrical energy is applied to restore some important property, like adsorption capacity or catalyst activity of a technical system. Electrochemical regeneration relies on principles of electrochemistry and relates to electrochemical processing. Electrochemical regeneration is conveniently conducted in situ with an electron as only reagent requiring simple handling and equipment. A technical setup for electrochemical regeneration requires in general two electrodes, an electrolyte and a power supply. In addition a membrane can be added to the setup in order to separate anode and cathode department. Some examples of electrochemical regeneration are electrochemical regeneration of activated carbon-based adsorbents in wastewater treatment and regeneration of enzymatic cofactors in electroenzymatic processes.

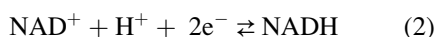
Organic pollutants in wastewaters can be removed by adsorption using, e.g., activated carbon as an adsorbent. This process is normally operated using a batch of adsorbent with sufficient capacity to operate for many months before reaching saturation. Once loaded, adsorbent must be disposed or regenerated. One option for adsorbent regeneration is electrochemical regeneration (Brown et al. 2004). The loaded adsorbent is located in a form of a packed or fluidized bed in the anode (anodic regeneration) or cathode (cathodic regeneration) compartment of the reactor. The efficiency of the regeneration depends on the processing time, voltage gradient, an electrolyte, and a compartment. According to literature the efficiency of cathodic regeneration is higher than of anodic regeneration. The mechanism of electrochemical regeneration is ascribed at the first place to local pH changes close to anode or cathode. At the anode side due to oxygen evolution reaction a pH decrease can be expected, while at the cathode side due to hydrogen evolution pH

value will increase. This pH changes induce organic pollutants desorption. In the next step, dissolved pollutants can be oxidized at the anode. In the case of the cathodic regeneration they have first to mitigate from the cathode to the anode. This might be mass transfer controlled leaving some residues in the cathode, unless very large currents or long regeneration times are employed.

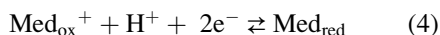
Further example of electrochemical regeneration is regeneration of enzymatic cofactors in electroenzymatic processes (Wichmann and Vasic-Racki 2005). Redox enzymes are very selective and specific catalysts, which can enable a number of partial oxidation or reduction reactions for industrial applications at mild conditions. Broader industrial application of redox enzymes has been so far hindered by their dependence on expensive cofactors (e.g., nicotinamide adenine dinucleotide (NAD)), which are consumed in the reaction (e.g., Eq. 1) and have to be regenerated for a process to be economical:



Electrochemical regeneration offers a possibility of cofactor regeneration. In this respect especially regeneration of NAD has been studied since NAD-dependent oxidoreductases are of great industrial interest. The electrochemical regeneration can be represented by this reaction:



This reaction is however not selective enough and the kinetics is very sluggish on most known electrode materials. Some improvements have been achieved by using surface-modified electrodes. Another strategy is to add an additional mediator according to



Electrochemical cofactor regeneration is still not a mature technology, and further improvements in electrode materials are needed to make this option feasible.

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Electrochemistry

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Electrochemistry is a branch of chemistry which studies charge transfer processes across an electrified interface also called an electrochemical double layer (Bockris and Reddy 1988, Hamann et al. 2007). Applications of electrochemistry are broad including electrochemical processing, electroanalysis electrochemical sensors, electrochemical regeneration, and corrosion. In addition, many important processes in biological systems like photosynthesis and cell respiration are inherently electrochemical processes.

The main feature of an electrochemical system is a separation of ionic- and electronic flows. Ions are flowing through the electrolyte which is exclusively an ionic conductor, while electrons flow through an outer electrical circuit which is exclusively an electron conductor. These two flows are interconverted at the electrode/electrolyte interface across the electrochemical double layer by means of an electrochemical reaction. The potential difference in the electrochemical double layer is related to thermodynamics (Nernst equation) and kinetics (Butler-Volmer or Tafel equations) of an electrochemical reaction and it is a driving force for the electrochemical reaction to take place. This unique feature of electrochemistry makes easy to control the reaction rate by electrons at different energies.

Electrochemical processes can be spontaneous (Gibbs free energy, $\Delta G < 0$), called galvanic, and

nonspontaneous $\Delta G > 0$, called electrolytic. Instead in terms of Gibbs free energy, spontaneity of an electrochemical process can be expressed in terms of cell voltage, where a positive value stands for a galvanic system and a negative for an electrolytic. The relationship between the cell voltage and Gibbs energy is given by equation $\Delta G = -nFU_r$, where n stands for number of exchanged electrons, F for a Faraday constant, and U_r for an equilibrium cell voltage.

Many electrochemical systems require presence of separators. This is usually a membrane which can be a permeable, termed diaphragm, or semipermeable, termed membrane. The latter type usually in addition to separation serves as an electrolyte, so-called solid electrolyte in electrochemical systems. An example is ceramic yttria-stabilized zirconia (YSZ) membrane which has found an application in solid oxide fuel cells. The ionic conductivity of this material is provided by O^{2-} ions.

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Electrodeionization

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Electrodeionization represents a variant of electrodialysis, modified in order to allow treatment of low-salinity and low-conductivity media. This technique is typically applied to produce high-purity water suitable for use, for example, in energetics. It combines the advantages of ion exchange with those of electrodialysis.

This technology is based on an electrodialysis unit with a diluate and also, in selected cases, a concentrate chamber filled with ion-exchanger particles. They can be arranged as monopolar beds (formed by particles of one polarity ion exchanger), as layered beds (cation- and anion-exchanger particles filled separately in several alternating layers), or as a mixed bed (uniform mixture of both types of ion-changer particles). The ion-exchange phase takes on the role of electroconductive media, thus reducing ohmic drop in the dilute chamber. At the same time it provides a three-dimensional interface for the removal of traces of ions present in the solution. Two regions are typically distinguished in the electrodeionization operation: (i) ions removal and (ii) solvent splitting. Within the first region the electrodeionization unit works below mass transfer limitation. It means, flux of ions to the solution – ion exchanger interface driven by the current load used has a value well below mass transfer limitation in a dilute chamber. The function of the ion-exchange bed consists in providing a pathway for ions trapped in the dilute channel to the ion-selective membranes separating dilute/concentrate chambers. In a second domain, however, the current load exceeds limiting current density, i.e. limiting flux of ions present from solution to the solution – ion exchanger interface. In such a case sufficient number of ions to transport corresponding electrical charge is provided by decomposition (dissociation) of the solvent (typically water). In contrast to electrodialysis, this splitting does not take place only at the solution-membrane interface but also at the contact of the cation- and anion-selective phase (Alvarado and Chen 2014).

In the case of a concentrate chamber, the role of the ion-exchange phase again consists in reducing ohmic drop in the channel while maintaining the concentration of the ions in the liquid phase at a minimum to reduce back diffusion from the concentrate to the dilute chamber.

The quality of the stream produced is comparable to that of the ion-exchange process. The advantage of electrodeionization is that it is a continuous process that does not require a regular regeneration phase of operation. This feature of

electrodeionization has a further important advantage. It saves a significant amount of corresponding chemicals and reduces the salinity of the waste streams produced. Such technology is thus a suitable component for closed loop technologies which, on ending, discharge removed salts in the solid form and avoids production of contaminated liquid streams.

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Electrodialysis

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The principle of electrodialysis is illustrated in Fig. 1 which shows a series of alternating anion- and cation-exchange membranes arranged between two electrodes. The membranes are separated by a spacer gasket and form individual cells, through which an electrolyte solution is pumped. When an electrical potential difference

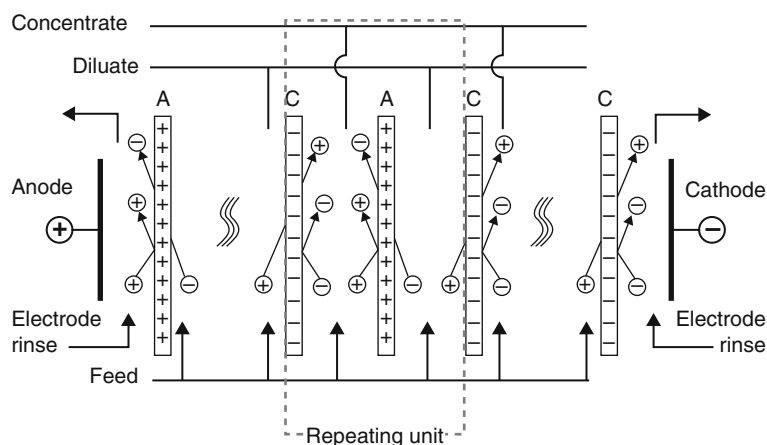
between the electrodes is established, the cations migrate toward the cathode. They pass through the cation-exchange membrane, but they are retained by the anion-exchange membrane. Likewise the anions migrate toward the anode and pass through the anion-exchange membrane but are retained by the cation-exchange membrane. The overall result is that an electrolyte is concentrated in alternate compartments, while its ion content is depleted in the other compartments. In an industrial size electrodialysis stack, 100–400 cell pairs are arranged between the electrodes. Various spacer and stack constructions such as the so-called sheet flow are used in practical applications (Schaffer and Mintz 1966).

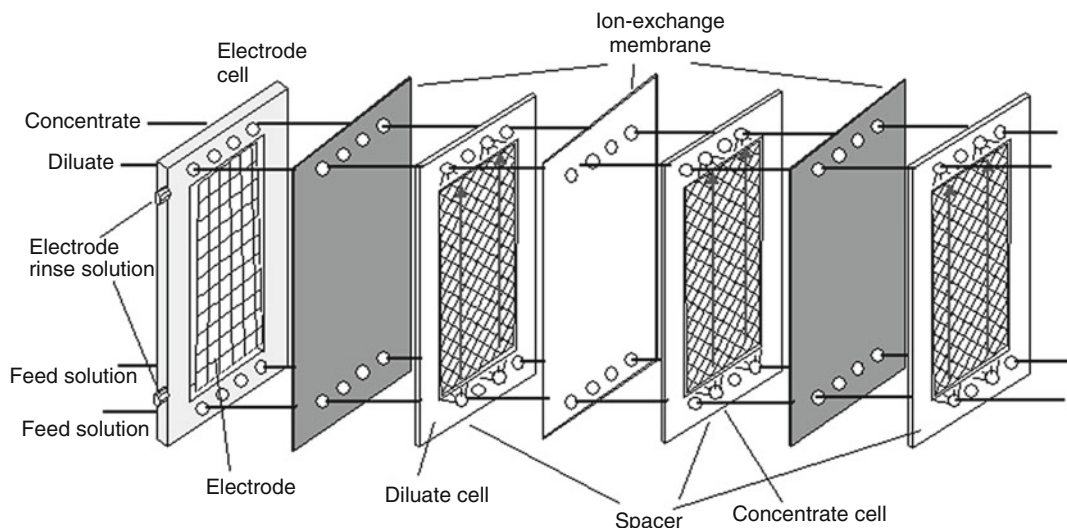
The concept of a sheet flow stack is illustrated in Fig. 2 which shows the arrangement of the spacers and membranes in a stack. The spacers not only separate the membranes and provide the proper mixing of the solutions in the cells, but in their frames, they also contain the manifolds for the two different flow streams in the stack.

Practical problems which affect the efficiency of electrodialysis are concentration polarization and membrane fouling. Concentration polarization which determines the so-called limiting current density is controlled by hydrodynamic parameters of the feed flow in the stack. Membrane fouling is controlled by a technique which is referred to as “clean in place” or electrodialysis reversal (Katz 1979).

The total costs in electrodialysis are the sum of the plant capital and the plant operating costs. The

Electrodialysis,
Fig. 1 Schematic diagram illustrating the principle of electrodialysis





Electrodialysis, Fig. 2 Schematic drawing illustrating the construction of a sheet flow stack design

capital related costs are proportional to the required membrane area for a given capacity plant and a for a given feed and product concentration. The operating costs are proportional to the required desalination energy which is the function of the transferred ions, i.e., the concentration difference between the feed and product ion concentration. The energy E^V required to desalinate 1 m^3 of water by electrodialysis is given by

$$E^V = \frac{Fr_{CP}^A}{\xi} i (C^f - C^p)$$

Here r_{CP}^A is the area resistance of the cell pair, which can be estimated from measurements of membrane resistance and conductivities of solutions, F is the Faraday constant, i is the current density, C^f and C^p are the feed and product water concentrations, and ξ is an efficient term which is generally close to 1.

Electrodialysis has advantages and limitations compared to other deionization processes such as reverse osmosis. A main advantage of electrodialysis compared to reverse osmosis is that very little feed pretreatment is required and higher brine concentrations can be achieved.

A major disadvantage especially for the production of potable water is the fact that only ions are removed, while uncharged components such as microorganisms or organic contaminants will not be eliminated. Another disadvantage of electrodialysis is the relatively high energy consumption when solutions with high salt concentrations have to be processed. Thus, electrodialysis can only be cost-effectively applied in water desalination in a certain range of feed water salt concentration and required product water (Strathmann 2010).

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Electrodialysis Reversal

► Reverse Electrodialysis (RED)

Electrodialysis Reversal in High Supersaturation Mode

► Reverse Electrodialysis in High Supersaturation Mode

Electrodialysis with Bipolar Membranes

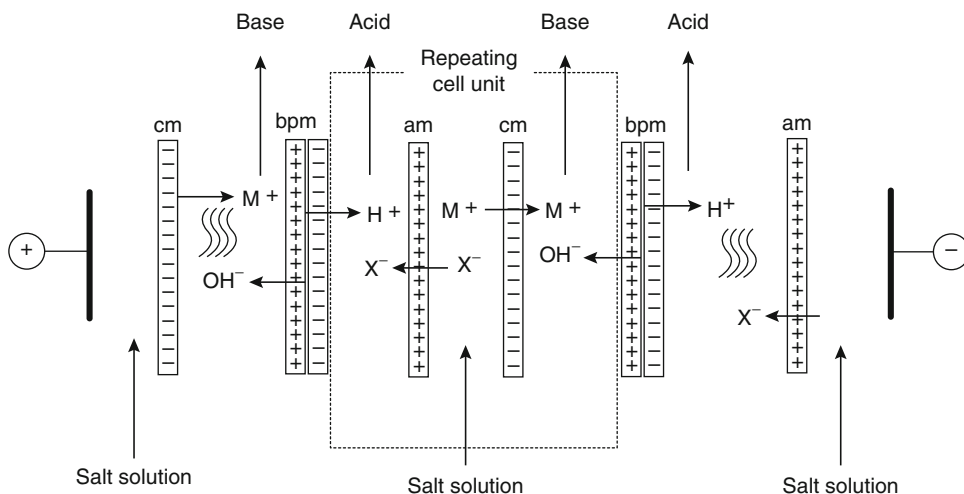
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The conventional electrodialysis can be combined with bipolar membranes and utilized to produce acids and bases from the corresponding salts. A bipolar membrane is a laminate of an anion on a cation-exchange layer. In this process monopolar cation- and anion-exchange membranes are installed together with bipolar membranes in alternating series in an electrodialysis

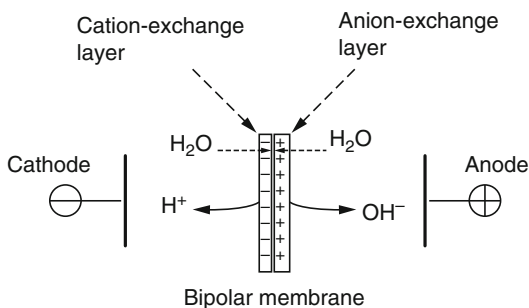
stack as illustrated in Fig. 1 which shows a typical repeating unit of an electrodialysis stack with bipolar membranes is composed of three cells, two monopolar membranes and a bipolar membrane. The outer cells of the repeating unit are fed with a salt solution, the inner cells with water, or a diluted acid and base. When an electrical potential gradient is applied across a repeating unit, protons and hydroxide ions which are generated in the bipolar membrane generate with the cations and anions removed from the salt solution, an acid and a base on either side of the bipolar membrane. The process design is closely related to that of the conventional electrodialysis using the sheet flow stack concept (Liu et al. 1977; Simons 1993).

The utilization of electrodialysis with bipolar membranes to produce acids and bases from the corresponding salts is economically very attractive and has a multitude of interesting potential applications in the chemical industry as well as in biotechnology and water treatment processes. Its key component is the bipolar membrane. The bipolar membrane schematically illustrated in Fig. 2 consists of a laminate of an anion- and a cation-exchange membrane with a 4–5 nm thick catalytic transition layer in between. In Fig. 2 this transition



Electrodialysis with Bipolar Membranes, Fig. 1 Schematic drawing illustrating the principle of the electrodialytic production of an acid and a base from the corresponding salt with bipolar membranes. Repeating

cell unit consisting of a cation-exchange membrane (cm), a bipolar membrane (bpm), and an anion-exchange membrane (am)



Electrodialysis with Bipolar Membranes, Fig. 2 Schematic drawing illustrating the electroalytic water dissociation in a bipolar membrane with water diffusing into the reaction region between the cation- and anion-exchange layers of the membrane and protons and hydroxide migrate to the corresponding electrode

layer has been artificially magnified. Water is diffusing through both membrane layers into the transition layer where it gets electro-catalytically dissociated into H^+ - and OH^- -ions, which migrate toward cathode and anode into the outer solutions.

The energy required for the water dissociation can be calculated from the Nernst equation for a concentration chain between solutions of different pH-values. It is given by:

$$\Delta G = F\Delta\varphi = 2.3RT\Delta\text{pH}$$

Here ΔG is the Gibbs free energy and ΔpH and $\Delta\varphi$ are the pH-value and the potential difference between the two solutions separated by the bipolar membrane. For 1 mol/L acid and base in the two phases separated by the bipolar membrane, ΔG is 0,022 kWh/mol and $\Delta\varphi$ is ca. 0,83 V at 25 °C. Compared to the ohmic potential drop over the membranes, the required potential drop for water splitting in the transition layer is much more pronounced. The determination of the costs for the production of acids and bases from the corresponding salts follows the same general procedure as applied for the cost calculation in electrodialysis desalination. The overall costs are the investment-related costs and the operating costs. The investment-related costs are dominated by the membrane costs and are proportional to the

required membrane area for a given capacity plant. They are a function of the current density applied in a given stack operation. A unit cell contains a bipolar membrane, a cation- and an anion-exchange membrane. The bipolar membrane is rather expensive, and its useful life time as well as that of the anion-exchange membrane is rather limited in strong bases. The operating costs in electrodialysis with bipolar membranes are strongly determined by the energy requirements which are composed of the energy required for the water dissociation in the bipolar membrane and the energy necessary to transfer the salt ions from the feed solution and protons and hydroxide ions from the transition region of the bipolar membrane into the acid and base solutions. The energy consumption due to the pumping of the solutions through the stack can generally be neglected. Since bipolar membranes became available as commercial products, a large number of applications have been identified and studied on a laboratory or pilot plant scale. However, in spite of the obvious technical and economical advantages of the technology, large-scale industrial plants are still quite rare (Gineste et al. 1996). The main reasons for the reluctant use of bipolar membrane electrodialysis are poor membrane stability at very high or low pH-values and insufficient permselectivity at high ion concentrations, which results in a substantial product salt contamination, low current efficiency, and short membrane life. Nevertheless, there are a number of smaller-scale applications in the chemical process industry, in biotechnology, in food processing, and in wastewater treatment.

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Electrodriven Membrane Processes

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Introduction

Electrolyte membranes or ion exchange membranes (IEMs) are ion-selective membranes for separation or charge transfer through the membranes. Electrodriven membrane processes employ IEMs under an electric field to perform (i) mass separation for concentration or dilution of ions in aqueous phase; (ii) chemical synthesis with an electrochemical reaction, such as chlorine-alkaline electrolysis and production of hydrogen via water electrolysis; and (iii) energy conversion and storage involving the conversion of chemicals into electrical energy and vice versa. Non-charged porous membranes are also used in some energy conversion processes to separate anolyte and catholyte solutions.

Separation Processes

Applications of the first type are mainly found in separation of ionic species under an electric field. Cations move toward a cathode and permeate through a cation exchange membrane while anions move toward an anode and permeate an anion exchange membrane. Due to rejection of non-permeable ion by the membranes, electrolytes are concentrated or diluted in a compartment. Typical processes in this category are electrodialysis, bipolar membrane electrodiagnosis, electrodeionization, and membrane capacitive deionization. Without an electric field, diffusion dialysis enables to purify acid or base solutions containing metallic contaminants.

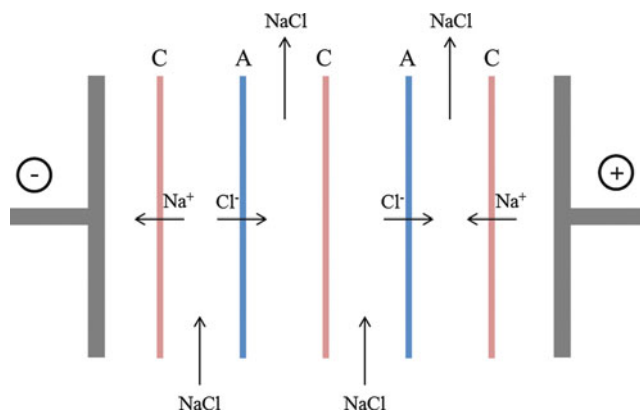
Electrodialysis (ED) is an electrochemical separation process using an electrical potential as a driving force. Electrodialysis systems typically consist of a cell arrangement with a series of

alternating anion and cation exchange membranes between an anode and a cathode. Within ion exchange membranes, charged groups are attached to the polymer backbone of the membrane material. These fixed charged groups partially or completely exclude ions of the same charge (co-ions) from the membrane, so that an anion exchange membrane (AEM) with fixed positively charged groups excludes positive ions but is freely permeable to negatively charged ions, referred to as counterions. Similarly, a cation exchange membrane (CEM) with fixed negatively charged groups is freely permeable to positively charged ions. When an aqueous salt solution is circulated in the cell under an electrical potential, the positively charged cations migrate toward the cathode and the negatively charged anions toward the anode. The overall result is a potential drop across the cell pairs as well as a change in the ion concentration in alternate compartments. The depleted solution is generally referred to as the diluate and the concentrated solution as the concentrate. Electrodialysis is used for desalination of various salt solutions including seawater as well as production of table salt (Fig. 1).

A **bipolar membrane (BPM)** in which the anion- and cation-exchangeable layers (AEL/CEL) are adjoined together easily splits water molecules into protons and hydroxyl ions under a reverse bias condition. Accordingly introduction of inorganic substances into the bipolar membrane is known to be an effective technique for generation of acid and base. Two or three compartment stack configurations may be chosen depending on the product specification, i.e., CEM-BPM, AEM-BPM, or CEM-BPM-AEM. It is expected that water-splitting electrodialysis using bipolar membrane can make zero-emission possible and be applied as a clean technology by recycling salt by-products after splitting to acid and base. Developments of high-performance bipolar membranes further expand use of bipolar membrane electrodialysis in chemical, biochemical, and environmental industries (Fig. 2).

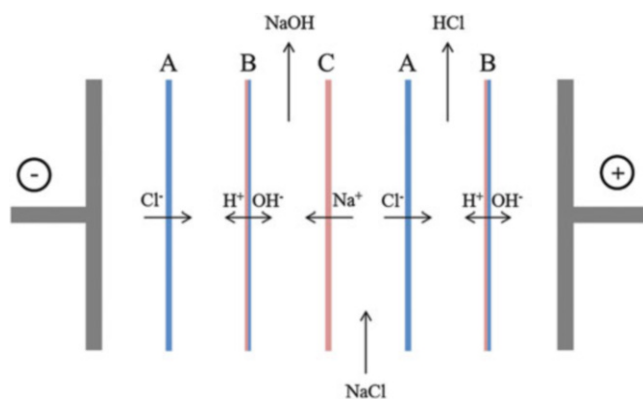
Electrodeionization (EDI) or continuous electrodeionization (CEDI) is a hybrid separation process that removes ionized species from liquids using electrically active media and an electrical

Electrodriven Membrane Processes, Fig. 1 An Electrodialysis Cell



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Electrodriven Membrane Processes, Fig. 2 A Bipolar Membrane Electrodialysis Cell

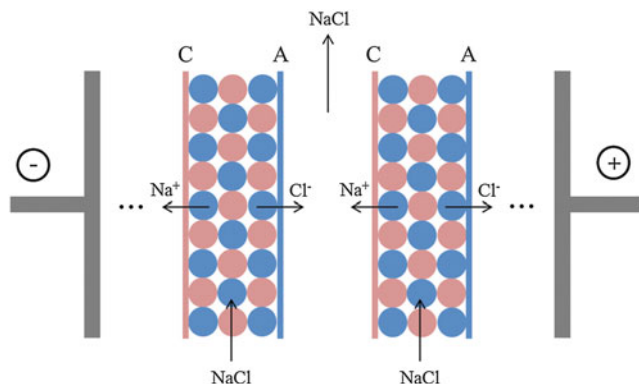


potential activating ion transport. The electrically active media, such as an ion exchange resin in CEDI devices, may function to alternately collect and discharge ionized species or to facilitate the transport of ions continuously by ionic or electronic substitution mechanisms. Unlike an ion exchange process, CEDI does not require chemicals to regenerate the ion exchange resin or concentrate the wastewater. In a CEDI system, the ion exchange resin bed plays a major role in the reduction of the high electrical resistance in the diluate compartment, while the ion exchange membranes lead to depletion and concentration of the solutions in the diluate and concentrate compartments, respectively. The CEDI process is capable of achieving high levels of purification

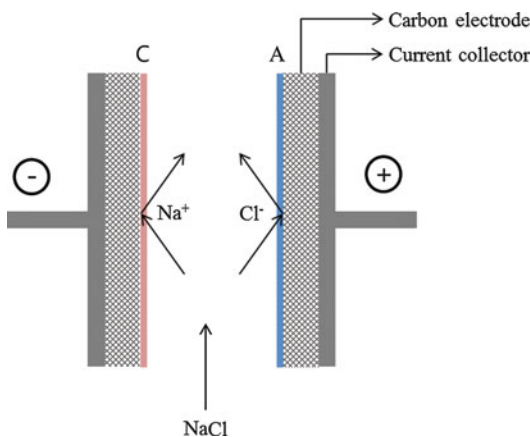
and the concentration of dissolved ionic solutes at a relatively low salt concentration (Fig. 3).

Membrane capacitive deionization (MCDI) is an advanced capacitive deionization (CDI) with the help of ion exchange membranes. A CDI system is operated by adsorption and desorption of ions on carbon electrodes. When an electric potential is applied to CDI cells, charged ions in contaminant water are adsorbed onto the surface of charged electrodes and forms an electric double layer due to the charged electrode and adsorbed ions, producing purified water. Often CDI leads to a higher energy consumption and a lower operation efficiency due to mobility of unwanted ions. To avoid this phenomenon, ion exchange membranes are introduced to CDI for ion selectivity,

Electrodriven Membrane Processes, Fig. 3 An Electrodeionization Cell

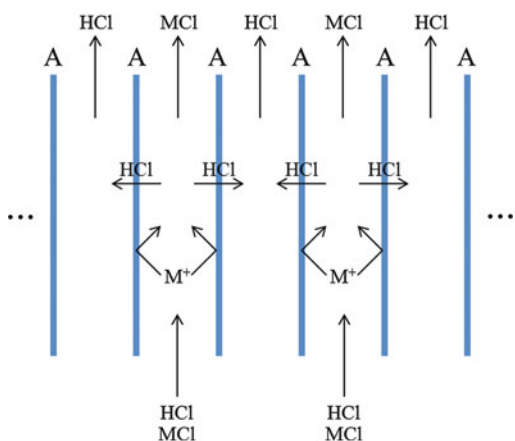


which is called membrane CDI (MCDI). A MCDI employs two types of ion exchange membranes, i.e., cation exchange and anion exchange membranes. The AEM and CEM are positioned in front of the positively and negatively charged electrodes, respectively. While counterions are attracted onto the electrode surface, simultaneously co-ions expelled from the counter electrode. The selectivity of ion exchange membranes prevents reverse adsorption and prohibits the mobility of unwanted ions.



Diffusion dialysis is a membrane separation process in which transport of selective ions is driven by a concentration difference over an ion exchange membrane. The diffusion dialyzer for acid recovery consists of a multitude of compartments made of gaskets arranged alternately with anion exchange membranes, which allow acids to permeate but retain metal salts. The gasket surrounds a meshlike spacer by which mixing in a

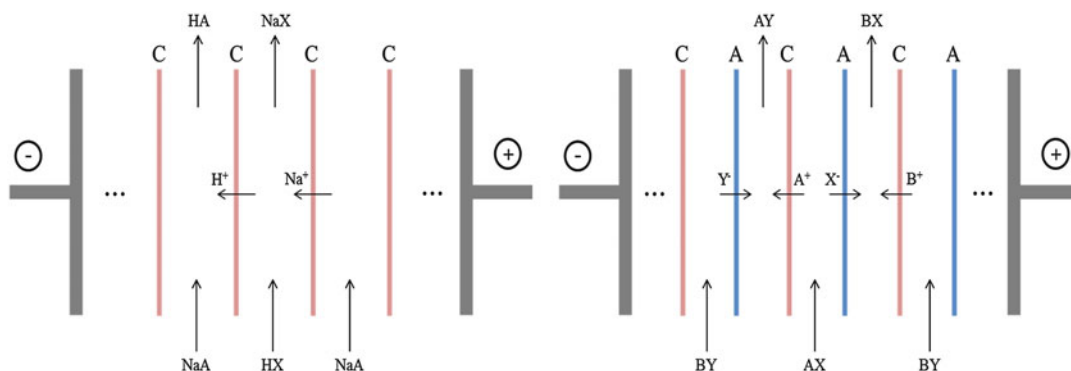
compartment is enhanced. The acid feed enters the bottom of every alternate compartment, as water is fed from the upper part of the stack to contact the acid feed counter currently. Permeate acids are collected from the bottom of the permeate compartment as purified acid product. The depleted feed flows out of the upper part as an effluent containing high concentrations of metal salts and a low concentration of remaining acid. Similarly a cation exchange membrane is used to recover base from metal salts.



Chemical Synthesis Processes

Applications of the second types are electrolysis processes to generate chemicals by electrode reactions and ion substitution through membranes.

A **chlor-alkali process** involves electrode reactions for the electrolysis of NaCl solution.



Electrodriven Membrane Processes, Fig. 4 A Membrane Capacitive Deionization Cell

The process produces caustic soda (NaOH) and chlorine (Cl_2) that are used in a wide range of industries. The most common chlor-alkali process is the electrolysis of aqueous sodium chloride in a membrane cell. The membrane is a cation permeable one which allows positive ions to pass through it. That is, the only the sodium ions from the NaCl solution may pass through the membrane and not the chloride ions. The advantage of the membrane process is that the sodium hydroxide solution is formed in a cathode compartment which is not contaminated with NaCl solution. Also purified NaCl should be supplied to obtain pure NaOH solution. Chlorine is generated at anode by oxidation of chloride ion. As a clean energy, hydrogen had been drawing more attention. One of hydrogen sources is electrolysis of water, splitting water to hydrogen and oxygen. Various catalysts and energy sources are investigated to improve the efficiency as a reverse process of a fuel cell.

Electro-ion substitution reaction can be carried out in an ED stack in which membranes are all of the same kind, either anion or cation exchange membranes. In a unit cell consisting of two compartments with CEMs, acid and feed streams flow. When an electric current is supplied to the stack, protons in the acid stream (HX) are transported to the feed stream (NaA) and convert the negatively charged organics (A^-) to free acid (HA). As a result the inorganic cations in the feed stream, in this case sodium ions, are transported to the acid compartment to meet the electroneutrality (NaX) in the feed stream, completing an ion exchange reaction,

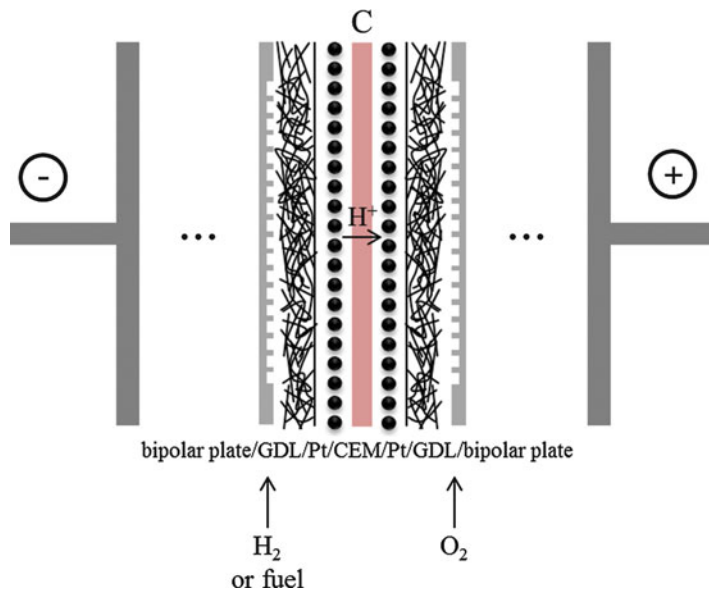
$\text{NaA} + \text{HX} \rightarrow \text{HA} + \text{NaX}$. A four-compartment double decomposition cell consists of a series of anion and cation exchange membranes arranged in an alternating pattern between anode and cathode. When the cell is operated with four different streams, ion substitution or salt metathesis reaction occurs, $\text{AX} + \text{BY} \rightarrow \text{AY} + \text{BX}$ (Fig. 4).

Energy Conversion Processes

Applications of the third types are found in various energy conversion and storage systems where charge carriers are selectively permeate through a membrane. Charge carriers are generated from electrode reactions or initially supplied as supporting electrolytes. When charge carriers move between anolyte and catholyte without mixing of active materials, a separator type membrane may be used. This type of applications includes fuel cell, lithium ion battery, redox flow battery, reverse electrodialysis, etc.

Polymer electrolyte fuel cells (PEFCs) are commonly considered to be one of the most likely potential alternative power sources due to their convenient operating temperature, high-energy conversion efficiency, and ease of integration into hybrid systems. Electricity is generated by potential difference between anode where hydrogen or fuel is oxidized to proton with the help of catalyst and cathode where oxygen is reduced and reacts with proton. A polymer electrolyte membrane is placed between the anode and cathode catalysts to insulate between electrodes. Polymer

Electrodriven Membrane Processes, Fig. 5 A
Diffusion Dialysis Cell



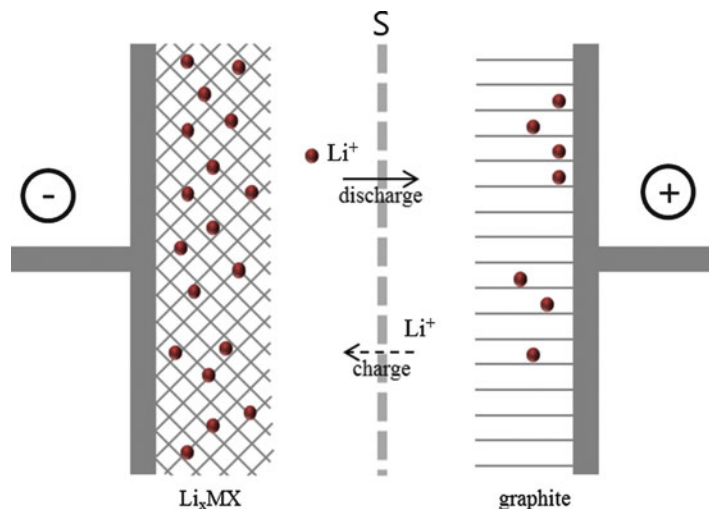
electrolyte membrane (PEM) sandwiched with two catalyst layers is called a membrane-electrode assembly (MEA). Perfluorinated sulfonic acid membranes such as Nafion[®], Flemion[®], Aciplex[®], and Dow[®] series have been widely used due to their high proton conductivity and good thermal and chemical stability. Hydrocarbon-based membranes, however, are generally less stable and subject to fast degradation, yet to be improved for practical applications. Recent efforts have focused on the commercialization of PEFCs in a range of applications, including use in portable devices, residences, stationary applications, and vehicles (Fig. 5).

A **lithium ion battery** is a rechargeable battery in which lithium ions move between anode and cathode with redox reactions during charge and discharge cycles. A separator is required to prevent mixing of anolyte and catholyte while lithium ions permeate freely in electrolyte solution. Often the separator is prepared as a multilayer porous membrane due to requirement of shutdown and meltdown. The lithium ion battery is rapidly growing due to the widespread use of wireless electronics such as cell phones and laptop computers. Moreover, concerns about global warming and oil shortages have led to the development of high energy density Li ion batteries

used for energy storages and electric vehicles. In these applications, safety is a key parameter. The safety of battery is closely linked to the battery separator absorbing a highly flammable liquid electrolyte. Although typical separators based on semicrystalline polyolefin materials such as polyethylene (PE) and polypropylene (PP) are mechanically strong and relatively inexpensive, their low melting temperature possibly causes physical contact between two electrodes over 180 °C. The physical contact triggers thermal runaway, which results in explosive burning of the highly flammable liquid electrolyte (Fig. 6).

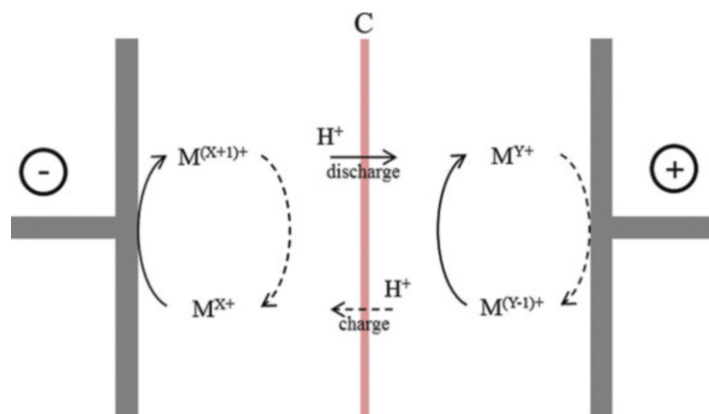
A **redox flow battery** is an energy storage device in which potential difference of a redox couple generates (discharge) or stores (charge) electric energy. Positive and negative electrolytes are stored separately and the electrolyte solutions are fed into a cell for energy conversion. A variety of membranes are used for RFB systems depending on the charge carrier, electrolyte solvent, and redox couple. Membranes must possess two main properties: preventing the undesirable cross-mixing of the negative and positive electrolytes to minimize self-discharge, while selectively conducting the charge carrier ions through the membrane to complete the redox circuit during the passage of current. Typically monovalent

Electrodriven Membrane Processes, Fig. 6 Electro-Ion Substitution Cell



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Electrodriven Membrane Processes, Fig. 7 A Salt Methathesis Cell

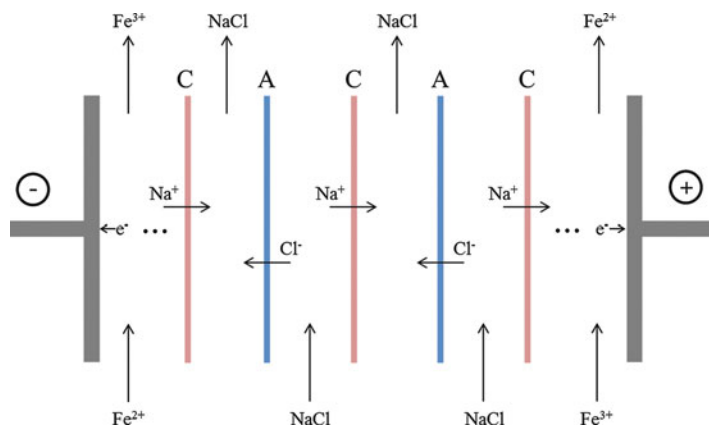


selective cation exchange membrane or a thin anion exchange membrane is used to prevent crossover of the cationic redox couples when proton is a charge carrier. A RFB is a promising technology due to several advantages such as its large capacity, convenient operating temperature, long cycle life, and so on. On the other hand, the use of an aqueous electrolyte severely restricts the energy density as is determined by the cell potential that is constrained by the electrochemical stability window of water. Along with commercialization of aqueous RFBs, nonaqueous RFBs which can offer a higher density have drawn considerable interest from energy storage

researchers. Furthermore, nonaqueous organic electrolytes provide a wider potential window of operation due to the high solubility of various metal–ligand complexes in an organic solvent. Nonaqueous RFB systems require ion exchange membranes or non-charged porous membranes depending on the electrochemical properties and molecular size of charge carriers employed (Fig. 7).

Reverse electrodialysis (RED) is an ion exchange membrane process for renewable energy generation. Electric potential occurs as a result of Donnan equilibrium where two solutions containing permeable ions are separated by a

Electrodriven Membrane Processes, Fig. 8 A
Polymer Electrolyte Membrane Fuel Cell



corresponding ion exchange membrane. Using a similar cell structure to electrodialysis, electricity can be generated by diffusion of ions using concentrated salt solution and diluted solution, called reverse electrodialysis (RED). Typically seawater and river water may be used as feed solution in a modified electrodialysis cell. Other salinity gradient power generation is pressure-retarded osmosis using pressure difference due to the concentration difference across an osmotic membrane including a polymer electrolyte active layer (Fig. 8).

Perspectives

Electrodialysis has been studied and industrialized for nearly a century as a leading electrodriven membrane process. Along with the appearance of advanced ion exchange membranes, various separation and reaction processes are following electrodialysis in many industries as demands for compact and environmentally friendly processes are growing continuously. Last several decades energy-related electrodriven membrane processes are growing rapidly with the help of membranes as a key component. Many membranes originally developed for separation processes have expanded their applications for energy conversion and storage. Accordingly the membranes should be characterized in terms of electrochemical properties to improve the performance appropriately,

i.e., ionic conductivity, transport number, oxidative stability, and power density.

Electroendosmosis

► [Electroosmosis, Overview of](#)

Electro-Fenton Process

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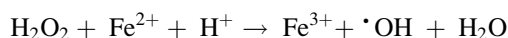
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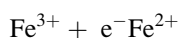
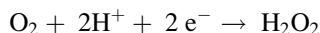
The electro-Fenton process is one of the most popular electrochemical advanced oxidation processes. As all the advanced oxidation process (AOPs), electro-Fenton (EF) process is based on the in situ production and reactions of the hydroxyl radicals ($\cdot OH$), the second powerful oxidant (after fluorine) with $E^0(\cdot OH/OH^-) = 2.80 \text{ V/SHE}$ and a very reactive species (Brillas et al. 2009; Oturan

and Aaron 2014). $\cdot\text{OH}$ is able to mineralize any organic pollutants and therefore used in AOPs in order for destruction of persistent organic pollutants.

Contrary to anodic oxidation process (Panizza and Cerisola 2009) in which $\cdot\text{OH}$ s are produced at anode surface from water oxidation (Panizza and Cerisola 2009), in the EF process, $\cdot\text{OH}$ s are generated in the bulk of solution from electrochemically assisted Fenton's reactions:



In the classical Fenton process, the Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$) is added externally to the reaction medium. This leads to the formation of $\text{Fe}(\text{OH})_3$ sludge and promotes wasting reactions that decrease process efficiency. EF process has a great advantage to generate in situ H_2O_2 (from two-electron reduction of O_2) and regenerate ferrous iron ions (from initially added catalyst) as schematized on the following electrochemical reactions:



There is no accumulation of Fe^{3+} and other reagents (H_2O_2 and Fe^{2+}), so sludge formation occurs and parasitic reactions are minimized to enhance mineralization (transformation of organics to CO_2 and water) efficiency.

In the case of using a high O_2 evolution anode such as boron-doped diamond (BDD) film anode, $\cdot\text{OH}$ are formed simultaneously at the anode as well as in the bulk solution from the electrogenerated Fenton's reagent. The oxidation power and mineralization efficiency are extremely high (Dirany et al. 2010).

The $\cdot\text{OH}$ thus formed by the process in a continuous and catalytic way will react with the organic pollutants present in the medium until

their mineralization, i.e., transformation to CO_2 , H_2O , and inorganic ions.

This EF process has been shown to be more efficient and cost-effective than some widely AOPs such as Fenton oxidation and ozonation for the treatment of organic pollutants species (Brillas et al. 2009; Oturan and Aaron 2014). It was successfully applied to the removal of toxic and persistent organic pollutants from water such as synthetic dyes, chlorinated aromatics, chloro-/nitrophenol herbicides, insecticides, fungicides and other pesticides, and pharmaceutical and personal care products. The results of these studies have shown that the EF process using a large surface area carbon-felt cathode is a very promising technology due to its simplicity, low cost, and outstanding performance, which is mainly due to the quick and efficient cathodic regeneration of the Fe^{2+} catalyst.

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Electrofiltration

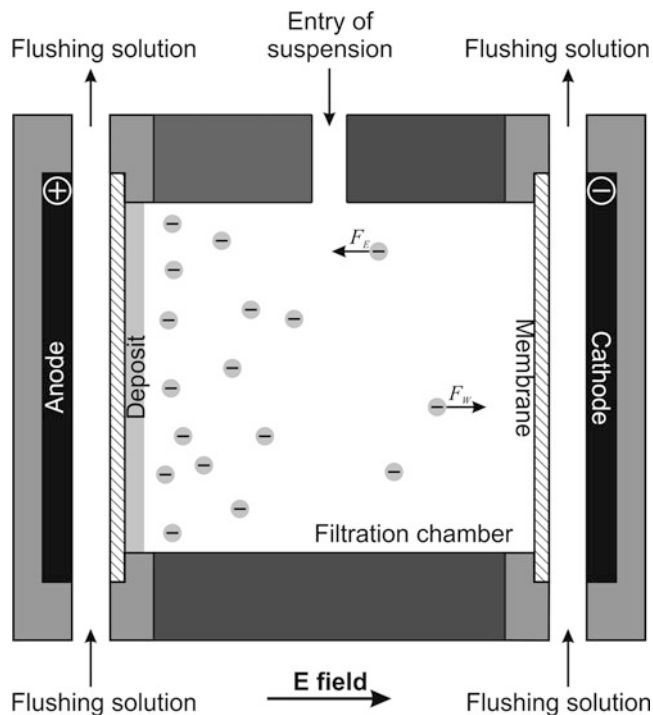
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Electrofiltration represents a modification of dead-end membrane micro- or ultrafiltration. It targets a significant reduction of the filtration

Electrofiltration,

Fig. 1 Schematic sketch of electrofiltration principle, F_w stands for driving force due to the friction between the particle and flowing solvent molecules and F_e stands for driving force resulting from action of the applied electric field E on the particle carrying electrical charge



time and focuses especially on the filtration and/or concentration of colloidal substances that otherwise rapidly build up a deposit of colloidal particles on the surface of the membrane, which strongly hinders permeation of the fluid phase. The basic principle is that colloidal particles usually carry an electric charge. Hence, by applying an appropriate electric field, colloidal particles can be moved in the direction opposite to the fluid flow, thus keeping the surface of the filtrating membrane free of the deposit (Henry et al. 1977). A schematic sketch of this arrangement is shown in the Fig. 1.

As the filtrating membrane remains unimpeded by a deposit of colloidal particles, the pressure drop across it remains relatively low. In contrast, the separator covered by the layer of colloidal particles attracted by the electric field does not permit a significant fluid flow. This results in a reduction of the shear stress forces in the deposited film of separated colloid. These facts make electrofiltration especially promising for the separation of biotechnology-derived products, the reason being that such products are typically sensitive to high shear stress forces while at the same

time they are electrically charged. The mild conditions of electrofiltration thus enable their properties to be preserved during the process of their separation (Gözke and Posten 2010).

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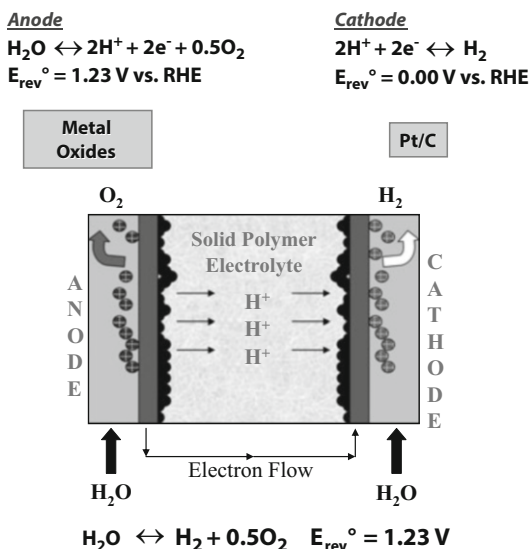
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Electrolyzers

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One of the main processes occurring in an electrolyzer device is the water electrolysis. Electrolysis of water is the dissociation of water molecules into hydrogen and oxygen gases. For this

process, in the presence of liquid water at 298 K and 1 bar, ΔG° is 237 kJ mol^{-1} (corresponding to $\sim 1.23 \text{ V}$), ΔS° is $163 \text{ J mol}^{-1} \text{ K}^{-1}$ ($T\Delta S^\circ \sim 0.25 \text{ V}$), whereas ΔH° is 286 kJ mol^{-1} . The thermoneutral potential at which this reaction occurs in the absence of external heat supply is $E_{\text{th},\Delta H} = 1.48 \text{ V}$ (upper heating value $3.54 \text{ kWh}\cdot\text{Nm}^{-3} \text{ H}_2$) (Millet et al. 2011). If steam is fed to the device, the reaction enthalpy is reduced by $\sim 40 \text{ kJ mol}^{-1}$ corresponding to the vaporization enthalpy. Water electrolysis is traditionally carried out in alkaline media with several commercial electrolyzers available on the market. Water electrolyzers using a solid polymer electrolyte are less common and generally use expensive materials such as noble metal electrocatalysts and Nafion membranes (Barbir 2005; Siracusano et al. 2010). Polymer electrolyte membrane (PEM) electrolyzers represent a viable alternative to alkaline electrolyzer using KOH or NaOH as electrolytes for hydrogen generation. The advantages of SPE water electrolyzers especially concern with increased safety, high energy density, and low maintenance. In the PEM water electrolyzer, water is usually supplied to the anodic compartment where oxygen evolution occurs, whereas hydrogen is produced at the cathode by protons transported through the protonic membrane (Fig. 1). The electrodes are usually composed of a platinum electrocatalyst for hydrogen evolution, whereas metal oxides (e.g., IrO_2 , RuO_2 , etc.) are used for the anode due to their enhanced activity and stability than Pt for this reaction (Marshall et al. 2007; Siracusano et al. 2010). The performance of an SPE electrolyzer is strongly related to the characteristics of the membrane and electrode assembly (MEA) where the electrochemical reactions take place at triple-phase boundary. Therefore, the interface between solid polymer electrolyte and electrocatalyst layers should be characterized by a suitable extension; furthermore, the contact resistance between the catalytic layer and the membrane should be as low as possible. Generally, Nafion[®] membrane is used as conducting polymer electrolyte in PEM electrolyzer systems. However, low levels of H_2 and O_2 crossover are necessary for PEMWE application due to the high-



Electrolyzers, Fig. 1 Principle of operation of a PEM water electrolysis cell

pressure operation that may reach 50–100 bars. Thus, a proper thickness is necessary for the polymer electrolyte separator (around $100 \mu\text{m}$). For high-pressure operation in PEM electrolyzers, reinforced PFSA membranes provide a proper combination of good conductivity and high mechanical strength.

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Electromembrane

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Electromembrane or “charged membrane” stands for ion-exchange membrane [IEM]. They are used in a number of processes which are rather different in their basic concept, their practical applications, and their technical relevance (Strathmann 2004). All IEM separation processes are based on the same fundamental principle which is the coupling of the transport of electrical charges, i.e., an electrical current with a transport of mass, i.e., cations or anions, through a permselective membrane due to an externally applied or internally generated potential gradient. There are two types of IEM: (i) monopolar and (ii) bipolar membranes.

Monopolar membranes are either cation-exchange membranes which contain negatively charged groups fixed to the polymer matrix or anion-exchange membranes which contain positively charged groups fixed to the polymer matrix.

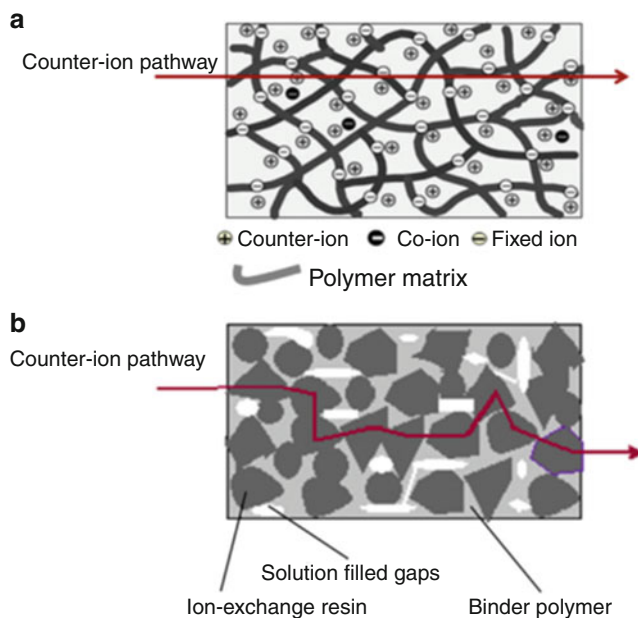
In a cation-exchange membrane, the fixed negative charges are in electrical equilibrium with mobile cations (counterions) in the interstices of the polymer as shown in Fig. 1 (Strathmann 2010). In this case, the mobile anions are referred to as coions. They are more or less excluded from the polymer matrix because of their electrical charge which is identical to that of the fixed ions (Donnan exclusion (Donnan 1911)). Thus, the selectivity of an IEM results from the exclusion of coions from the membrane phase. The properties of IEM are determined by different parameters such as the density of the polymer network, the hydrophobic/hydrophilic character of the polymer matrix, the nature and the ratio of fixed ion-exchange groups, the cross-linking ratio, etc.

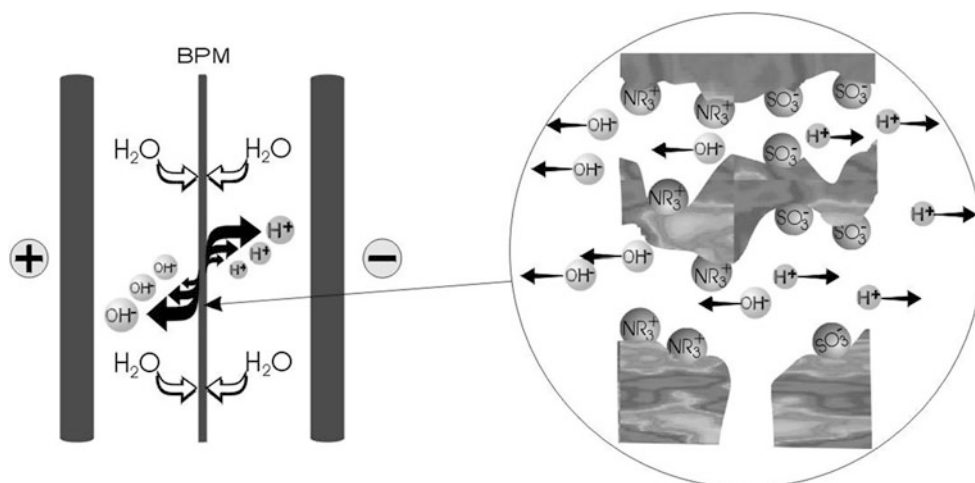
The most desired properties of IEM are (i) high chemical and thermal stabilities, (ii) high mechanical and dimension stabilities, (iii) high permselectivity, (iv) low electrical resistance, (v) and a low cost.

Bipolar membranes (BPMs) are composed of two layers of ion exchangers joined by a hydrophilic junction (Pourcelly et al. 2009). The diffusion of water from both sides of the BPM allows its dissociation under the electrical field to generate protons and hydroxyl ions, which further

Electromembrane,

Fig. 1 (a) Cation-exchange membrane with a homogeneous structure; (b) ion-exchange membrane with a heterogeneous structure prepared from an ion-exchange resin powder in a binder polymer (From Strathmann 2010)





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Electromembrane, Fig. 2 Principle of a bipolar membrane. *Left hand:* water dissociation under electrical field. *Right hand:* the two ion-exchange layers bearing fixed anion- or cation- exchange groups

migrate from the junction layer through the cation- and anion-exchange layers of the BPM as depicted in Fig. 2. The requirements for suitability of BPM include that for monopolar membranes but also an experimental potential to achieve the water-splitting capability as close as possible as the theoretical value equal to 0.83 V at 25 °C.

Nowadays, superior styrene-divinylbenzene copolymer membranes can be easily purchased, perfluorinated membranes with great chemical stability are on the market, and BPM with an industrial-scale lifetime (>20,000 h) is available.

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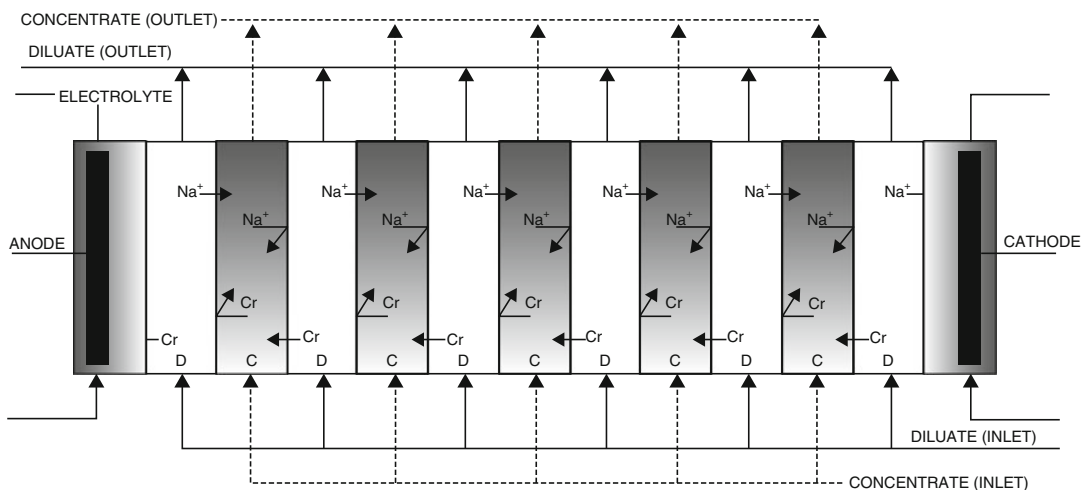
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Electromembrane Processes

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Electromembrane processes involve ion-exchange membranes. They can be divided into three types: (i) Separation of components such as salts or acids and bases from electrolyte solutions. In this case, the driving force for the ion transport across the membrane is an electrical potential as in electrodialysis or a concentration gradient as in both diffusion dialysis and Donnan dialysis. (ii) The second type of processes involves an electrochemical reaction producing chemicals such as chlorine, acids and bases, or organic and inorganic compounds. The most known process of this type is the chlorine-alkali production where the ion-exchange membrane is the key component. (iii) The third type of ion-exchange membrane processes involves the conversion of chemical into electrical energy and vice versa. The solid polymer electrolyte fuel cell is the most significant application (Strathmann 2004).



Electromembrane Processes, Fig. 1 Scheme of a conventional two-compartment electrodesialysis stack (C): concentrate, (D): diluate compartments

(i): In dialysis, the driving force for the component transport is a difference of concentration between the two solutions separated by a membrane. In diffusion dialysis and Donnan dialysis the driving force is also a concentration gradient but the membrane is carrying anions or cations according to its permselectivity. Diffusion dialysis with anion exchange membranes is used on a large scale to recover acids from pickling solutions (Kobuchi et al. 1987). Donnan dialysis is used for water softening or for recovering organic acids from their salts (Kliber and Wisnieski 2011).

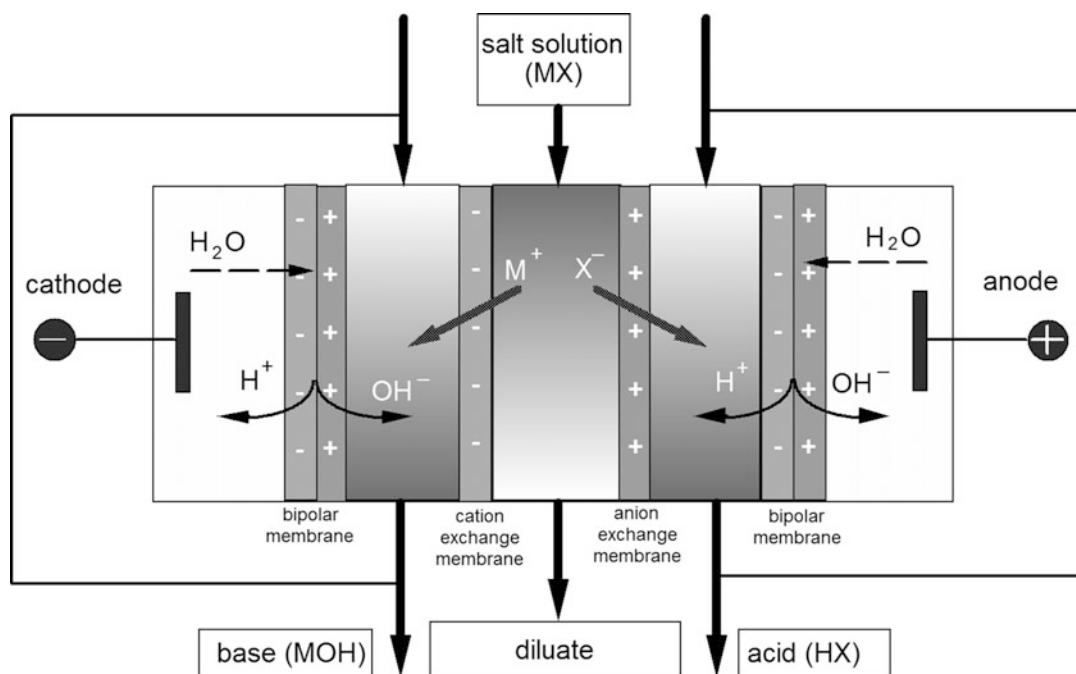
Electrodialysis (ED) is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. The elementary cell consists of a feed (diluate) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes. In almost all practical ED processes, multiple ED cells (few hundreds) are arranged into a configuration called an ED stack Fig. 1.

Conventional ED is used mainly for desalination of saline solutions (chemicals) or milk whey (food industry). It can be combined with bipolar membranes (bipolar membrane electrodialysis)

and used to produce acids and bases from their corresponding salts, Fig. 2. This process is economically very attractive and has several interesting potential applications mainly in food industry, fine chemicals, or biotechnologies (Pourcelly et al. 2009).

(ii): The most known membrane electrolysis processes are for the production of chlorine and caustic soda (Pletcher and Walsh 1990) or special organic compounds (Sata 1991). In the chlorine-alkali process, the cells are arranged in a similar way as in an electrodesialysis stack but in two different configurations using monopolar or bipolar electrodes. Due to the severe operating conditions (80 °C, 35 wt% NaOH, wet chlorine), the membrane is a composite structure of sulfonated and carboxylated perfluorinated reinforced polymers.

(iii): Ion-exchange membranes are used today also as key components in energy storage and conversion systems such as batteries and fuel cells. A fuel cell is an electrochemical reactor in which energy is converted into electrical energy. Generally fuel cells are fed with hydrogen which is transformed into protons at a catalytic anode with electrons. Protons then migrate across a proton conducting membrane and combine with oxygen to produce water at the catalytic cathode (Lucia 2014).



Electromembrane Processes, Fig. 2 Electrodialysis with bipolar membrane. Scheme of a three-compartment cell

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Electroosmosis

Karel Bouzek

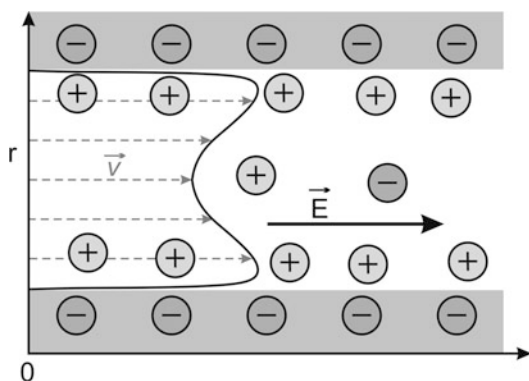
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Electroosmosis is the term used for the convective flow of a solution containing charge carriers, e.g., in the form of dissociated salts, through the pores or structure of a material with an electrically charged internal surface. In the field of membrane processes, this phenomenon is typically discussed in connection with the utilization of ion-selective membranes under current load. However, it can potentially occur in any membrane material. The schematic sketch of the principle of electroosmotic flux initiation in an ion-selective membrane pore (void space) is shown in Fig. 1.

The driving force of electroosmotic flux is the electric field. Flux velocity is directly proportional to the hydraulic permeability of a membrane and

Electronic and Ionic Conductivity

► Mixed Conducting Membranes



Electroosmosis, Fig. 1 The schematic sketch of a principle of electroosmotic flux initiation in the membrane with an electric charge carriers fixed on the pore (void fraction) wall

indirectly proportional to the viscosity of the pore fluid. The latter parameter represents an excess of free charge carriers of one sign in the bulk of the pore fluid. An excess of one-sign charge carriers is possible on account of an intrinsic property of an ion-selective membrane, i.e., the presence of charge-carrying functional groups in the membrane structure. These ion groups are bonded by a covalent bond to the backbone of the membrane material. They are thus fixed and immobilized in the structure. In the case of conventional membrane materials, the role of fixed charge can be carried out by ions specifically adsorbed on the pore walls or along the backbone of membrane materials. The charge carried by functional groups and/or adsorbed in the internal structure of the membrane has to be compensated by an excess charge of opposite sign present in the pore fluid. The electroosmotic convective flow of the pore fluid is induced by friction force between the solvated mobile charge carriers (ions) moving under the action of the electric field and the surrounding liquid phase molecules (Squires and Bazant 2004).

Electroosmotic flux represents one of the mechanisms of mass transfer through an ion-selective membrane. Its significance increases with increasing current load and, thus, the intensity of the electric field applied across the membrane (Fila and Bouzek 2008).

Cross-References

► [Electroosmosis, Overview of](#)

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Electroosmosis, Overview of

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Synonyms

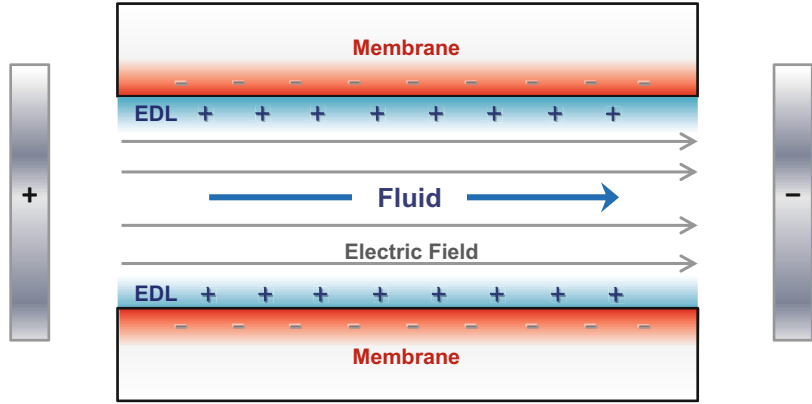
[Electroosmosis](#); [Electroendosmosis](#); [Electro-osmosis](#); [Electroosmotic flow](#); EOF

Electro-osmosis is the movement of liquid in response to an applied electric field across a conduit such as a membrane, capillary tube, microchannel, or porous material.

The application of an external electric field near a solid/liquid interface may result in the motion of liquid with respect to an adjacent charged surface. These associated effects are known as electrokinetic phenomena (Hunter 1981), first observed by Reuss in 1808 (Reuss 1809). Electrokinetic phenomena include electro-osmosis, electroacoustics, electrophoresis, diffusiophoresis, streaming potential, zeta potential, and sedimentation potential. The earliest experiments on electrokinetic phenomena focused on electro-osmosis because these are the easiest to conduct (Wall 2010). Early investigators included Wollaston, Porrett, Napier, Faraday, and Daniell.

Electroosmosis, Overview of,

Fig. 1 Schematic representation of electro-osmosis in a membrane pore, showing the effect of the electric field on the electric double layer (EDL) and the resulting drag on the bulk fluid



In electro-osmosis, the bulk fluid moves relative to a charged surface due to an external electric field.

The chemical equilibrium between a solid surface (such as a membrane) and a fluid containing charged species typically leads to the interface acquiring a net fixed electrical charge (most often negative for membranes), characterized by the zeta potential (ζ). The presence of co-ions (similarly charged ions) and counterions (oppositely charged ions) results in attraction and repulsion of ions in the vicinity of a charged surface. This phenomenon, coupled with the random thermal motion of the ions, creates an electric double layer (EDL) or Debye layer in the region near the interface. Electroneutrality is not maintained within the EDL, because there is an excess of counterions compared to co-ions in order to neutralize the surface charge (Probstein 2005). When an electric field is applied to the fluid, the net charge in the electrical double layer is induced to move by the resulting Coulomb force. The movement of ions drags bound solvent, causing bulk fluid motion due to momentum transfer, as depicted in Fig. 1. The resulting flow is termed electro-osmotic flow. Electro-osmosis can only occur if there are charged species in the fluid that can respond to the electric field (Jagannadh and Muralidhara 1996).

Electro-osmosis can be described mathematically using the momentum transport equation, as the resulting body force due to an electric field on a charged fluid (Hu and Li 2007). The net charge density of the fluid (ρ_e) can be related to the

electric potential (ϕ) and the permittivity of the fluid (ϵ) by Poisson's equation:

$$\epsilon \nabla^2 \phi = -\rho_e \quad (1)$$

Under negligible convective or electrophoretic-induced flow, the charge density follows a Boltzmann distribution (Hunter 1981), and the charge density can be obtained by solving the nonlinear Poisson–Boltzmann equation:

$$\nabla^2 \phi - \kappa^2 \sinh(\phi) = 0 \quad (2)$$

where the constant κ depends on the ionic composition (Russel et al. 1989). Although solutions to Eq. 2 can only be obtained numerically for complex geometries, it can be linearized using the Debye–Hückel approximation, which leads to the following electric potential distribution:

$$\phi = \zeta \exp\left(\frac{-y}{\lambda_D}\right) \quad (3)$$

where y is the distance from the surface, and $\lambda_D = 1/\kappa$ is the Debye length.

In membrane systems, electro-osmosis can be approximated through the Helmholtz–Smoluchowski (HS) velocity equation:

$$u_s = -\frac{\epsilon \zeta E_x}{\mu} \quad (4)$$

The HS approximation described by Eq. 4 is an artificial slip velocity implemented on a charged

surface. It can be used to simulate the effect of electro-osmosis on the velocity in a conduit at the outer edge of the EDL (Probstein 2005). This equation implies that the electro-osmotic flow velocity is proportional to the applied electric field. Other equations that are relevant to electro-osmosis under different conditions include the Hückel–Onsager equation and the Henry equation.

Most common applications of electro-osmosis are in capillary electrophoresis, capillary electrochromatography, and microfluidic devices in fields as diverse as biophysics, dewatering, geomechanics, medicine, microchips, oil and gas production, and separations including in membrane separation. There are a number of important applications in membrane technology. At the fundamental level, electro-osmosis can be used to determine the zeta potential of membranes (Bowen and Clark 1984). It can also be beneficial for the operation of membrane separation systems, and has found numerous applications in microfiltration and ultrafiltration processes (Bowen 1993), in particular to do with the mitigation of membrane fouling. This is because surface activity and membrane charge, two phenomena closely related to membrane fouling, cannot be influenced through hydrodynamic forces such as increased shear. Electro-osmosis can be used for membrane cleaning and restoration (Bowen et al. 1989), for backwashing (Bowen and Sabuni 1994), for releasing filter cakes in dead-end membrane processes (Bowen and Ahmad 1997), and for enhancing flux (Sarkar and De 2010).

Although the use of DC electric fields in membrane separation processes has been in practice for several decades, anode corrosion is a significant problem that has discouraged its wider application (Jagannadh and Muralidhara 1996). Nevertheless, the development and availability of corrosion-resistant materials has enabled recent developments and commercialization of these techniques. Electro-osmosis has also found applications in RO processes, leading to improved recovery through membrane backwashing (Spiegler and Macleish 1981) or by increasing the level of mixing in the boundary layer (Liang et al. 2014).

Cross-References

- [Backwashing](#)
- [Electrical Double Layer](#)
- [Electroosmotic Drag in Membranes](#)
- [Membrane Fouling](#)
- [Surface Charge Density](#)
- [Zeta Potential](#)

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Electroosmotic Drag Flux

► Electroosmotic Drag in Membranes

Electroosmotic Drag in Membranes

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Synonyms

Electroosmotic drag flux; Electroosmotic water transport; EOD

Electroosmotic drag in membranes refers to the movement of water or other electroneutral solvents through a membrane, associated with the movement of ions under the influence of an electric field.

The zeta potential at the interface between a membrane and an electrolyte generally leads to the creation of an electric double layer (EDL). When an electric field is applied to fluid within an EDL, the net charge is induced to move by the resulting Coulomb force. The movement of ions drags bound solvent, causing bulk fluid motion

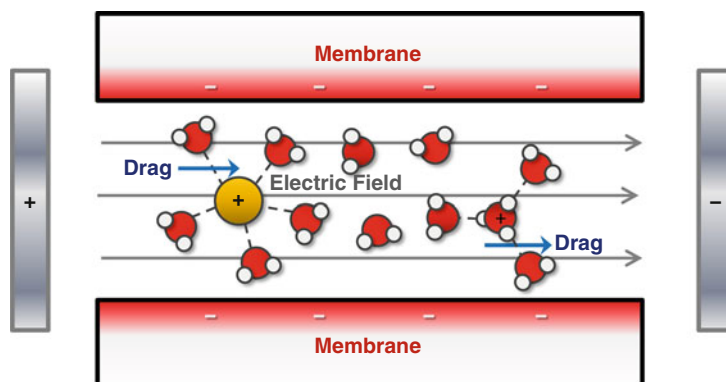
due to momentum transfer (viscous drag). This bulk fluid motion due to an external electric field is termed electroosmosis (De Groot 1966) and can occur in any fluid with a net charge, including in membrane channels or within membrane pores (Fig. 1).

Electroosmotic drag (EOD) is the underlying mechanism responsible for solvent transport in a number of membrane techniques including:

- EOD in electrodialysis (ED), often called “water transport,” is one of the reasons for losing current density (Indusekhar and Krishnaswamy 1965). ED has many industrial applications including the production of chlorine, NaOH, and other inorganic acids and bases (de Groot et al. 2011).
- EOD of water in proton exchange membranes (PEMs, also referred to as polymer electrolyte membranes), which leads to water management issues (Zawodzinski et al. 1995).
- EOD of methanol in direct methanol fuel cells (DMFCs), leading to methanol crossover (Heinzel and Barragán 1999).
- In vanadium redox batteries (VRBs), EOD can cause vanadium crossover and capacity loss (Agar et al. 2013).
- EOD in electroosmotic pumps (EOPs) is used to generate flow or pressure (Wang et al. 2006). EOPs can be used to aid with the hydration of PEMs for fuel cells.
- EOD is a mechanism for producing anomalous flux through charged membranes (e.g., NF membranes) due to the selective

Electroosmotic Drag in Membranes,

Fig. 1 Schematic representation of electroosmotic drag in a membrane pore. The electric field causes the dissolved ions to experience a net force, and these ions transfer momentum to the solvent molecules through viscous drag



passage of one type of charged ion over the other, leading to the axial rearrangement of the EDLs (Sasidhar and Ruckenstein 1982).

EOD is of particular importance in PEMs such as Nafion[®] and sulfonated polyetherketones, used in fuel cells and VRBs. Water management critically impacts the performance of PEMs for fuel cells, as their proton conductivity increases with hydration. Too little water can dry the membrane, leading to a reduction in conductivity and consequently lower cell performance. Too much water can flood the membrane and lead to cathode flooding problems. In addition to the generation of water at the cathode catalyst layer due to the electrochemical reaction, water is also transported through the membrane (Lee et al. 2008). The permeate flux of water in a PEM is governed by two main mechanisms: (a) the osmotic flux due to a chemical potential gradient across the membrane, which is influenced by both the activity of the solution (osmotic pressure) and the hydrostatic pressure, and (b) the electroosmotic flux due to the drag induced by the proton flux (Ren and Gottesfeld 2001).

In order to optimize water concentration in a fuel cell membrane, it is important to quantify electroosmotic drag. The electroosmotic water flux can be related to the proton flux through the membrane by means of the electroosmotic drag coefficient (ps_{drag}), which is defined as the number of water molecules transported through the membrane per proton as the chemical potential gradient of water tends to zero (Ise et al. 1999).

Cross-References

- Direct Methanol Fuel Cell (DMFC)
- Electrical Double Layer
- Electrodialysis
- Polymer Electrolyte Membrane Fuel Cell (PEMFC)
- Proton-Exchange Membranes for Fuel Cells
- Zeta Potential

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Electroosmotic Flow

- [Electroosmosis, Overview of](#)

Electroosmotic Water Transport

- [Electroosmotic Drag in Membranes](#)

Electrooxidation

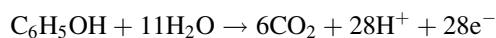
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Electrooxidation is a direct anodic oxidation technique to remove biorefractory pollutants by direct electrolysis in which pollutants exchange electrons with the anode surface without intermediate substances. It differs from indirect anodic oxidation. Indeed by indirect anodic oxidation, pollutants are oxidized by $\cdot\text{OH}$ s radicals generated by water oxidation on a high O_2 evolution anode such as boron-doped diamond (BDD).

Direct anodic oxidation is possible using noble metals (Pt and Pd), metal oxide (IrO_2 , PbO_2), or carbon-based (boron-doped diamond) anodes, before oxygen evolution. The first stage is the pollutant adsorption on the anode surface. The second stage is the oxygen (as a source of electrons) transfer from water to the organic pollutant using electric energy (i.e., anodic polarization) through the so-called electrochemical oxygen transfer reaction (EOTR). A typical example of EOTR often cited in the literature (Panizza and Cerisola 2009) to illustrate direct electrooxidation is anodic incineration of phenol as follows:



The complete phenol oxidation to CO_2 (i.e., mineralization) is obtained at the anode, and protons liberated in this reaction are reduced at the cathode to hydrogen. The pollutant mineralization rate depends mainly on the nature of the anodic material, the choice of the anodic potential (fixed before oxygen evolution), and chemical and physical parameters such as electrolyte and pollutant composition and concentration and temperature.

The main limitation of electrooxidation is the decrease of the electrocatalytic activity of the electrode because of the fast formation of a polymer layer from oxidation intermediates on the anode surface. Film formation depends on the adsorption properties of the electrode surface, the concentration and the nature of organic compounds, their degradation intermediates, the presence of oxygen, etc. Then electrodes presenting a surface with weak adsorption properties are promoted to gain in stability (Panizza and Cerisola 2003). Nevertheless, in anaerobic conditions, the formation of the polymer fouling layer remains the limiting factor of the mineralization.

To overcome this poisoning effect, anode must be polarized over oxygen evolution to promote water discharge, leading to hydroxyl radical ($\cdot\text{OH}$) formation on specific electrode like boron-doped diamond. The electrochemical formation of this powerful oxidant avoids then polymer fouling layer formation and then the decrease of the electrocatalytic activity of the electrode. More details can be found concerning this electrochemical advanced oxidation process (EAOP) in the entry “indirect anodic oxidation.”

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Electrophoresis

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The term electrophoresis refers to the motion of suspended particles in an applied electric field. Among separation techniques, electrophoresis is

widely used in research and development and quality control in disciplines such as biochemistry, immunology, genetics, and molecular biology (Westermeyer 2001). Electrophoresis is based on the differential migration of charged species in a semiconductive medium under the influence of an electric field. Separation of many different kinds of species including proteins, DNA, nucleotides, drugs, and many other biochemicals is obtained upon differences in size, charge, and hydrophobicity. The technique was first reported in 1937 by Arne Tiselius who won the Nobel Prize in Chemistry in 1948 for the separation of different serum proteins by a method called “moving-boundary electrophoresis.” Since then, a number of improved techniques have been introduced such as gel electrophoresis, capillary electrophoresis, and two-dimensional electrophoresis.

Gel electrophoresis uses an electric current passed through an agarose or polyacrylamide gel (SDS-PAGE) to separate the molecules in a sample on the basis of their differences in molecular size and charge. As the sample migrates in the gel in response to the electric current, the smaller species move more quickly than the larger species, which results in a distinct banded pattern in the gel. This banded pattern may be visualized via the application of staining agents, such as ethidium bromide, which reveals the gel bands under UV light, or silver stain, which is typically used to detect proteins. The silver stain is compatible with mass spectrometry techniques for further analysis of the protein composition. Capillary electrophoresis (CE) involves a combination of both polyacrylamide gel electrophoresis (SDS-PAGE) and high-performance liquid chromatography (HPLC) (Ahuja and Jimidar 2008). High voltages of 500 V/cm or greater are generated within narrow capillaries (20–200 μm). The high voltages cause electroosmotic and electrophoretic movement of buffer solutions and ions, respectively, within the capillary. Two-dimensional gel electrophoresis (2-D electrophoresis) separates species in two steps, according to two independent properties. In a common technique, the first dimension is isoelectric focusing, which separates proteins according to their isoelectric points; the second dimension is SDS polyacrylamide gel electrophoresis

(SDS-PAGE), which separates proteins according to their molecular size. The method involves placing the sample in gel with a pH gradient and applying a potential difference across it.

Cellulose acetate membranes are other current supporting media for electrophoresis separation (Westermeyer 2001). They are used for routine clinical analysis and related applications, as well as for the analysis of molecules in physiological fluids. These membranes have large pores and therefore have a low sieving effect on molecules. The electrophoretic separation is thus entirely based on charge density. The matrix exerts little effect on diffusion so that the separated zones are relatively wide and the resolution and limit of detection area is low. For these reasons, cellulose acetate membranes are often replaced by gel electrophoresis.

Other supporting membranes for electrophoresis include Nafion membranes, a type of perfluorosulfonic acid membrane, and cation-exchange membranes, which are chemically resistant and consist of a pore-structure cluster network (Fang et al. 2004). These membranes are widely used in the field of chloralkali industry and in fuel cells. A Nafion membrane contains hydrophilic pores (10–20 Å and 50–60 Å in size) acting as very narrow electrophoresis channels. The fixed-charge sites ($-\text{SO}_3^-$) on the hydrophilic pore surface provide a strong charged background. Nafion membrane electrophoresis is a potentially attractive technique for the separation of small organic molecules like amino acids or ions.

Cross-References

► Ion-Exchange Membranes

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Electrophoretic Deposition

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Electrophoretic deposition (EPD), also called electrocoating, e-coating, cathodic electrodeposition, or electrophoretic coating, is a simple and effective technique for coating of charged particles on substrates (Besra and Liu 2007). It has several advantages including continuous processing, uniform deposition and control of the thickness, and morphology of a deposited film by adjustment of the deposition time and applied potential. In EPD, charged powder particles, dispersed or suspended in a liquid medium, are attracted and deposited onto a conductive substrate of opposite charge on application of a DC electric field. There are two types of electrophoretic deposition (Fig. 1). When the particles are positively charged, the deposition happens on the negative electrode (cathode) and the process is termed cathodic electrophoretic deposition. The deposition of negatively charged particles on positive electrode (anode) is called anodic electrophoretic deposition. By suitable modification of the surface charge on the particles, any of the two modes of deposition is possible. This technique is convenient for stable suspensions containing charged particles free to move when an electric field is applied. Therefore, EPD can be applied to any material that is available as a fine powder (e.g., $<30\ \mu\text{m}$ particle size) or as a colloidal

suspension, including metals, polymers, ceramics, and glasses.

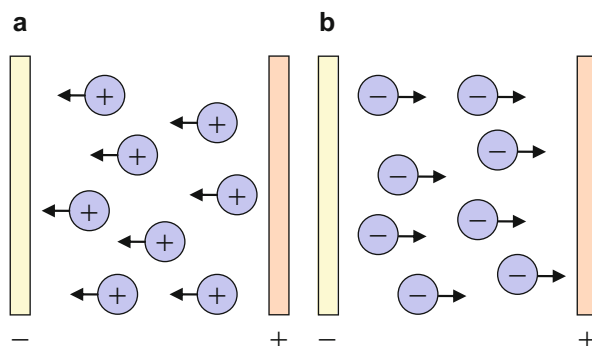
The fundamental mechanisms of EPD are described in the literature mainly in the framework of the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and in relation to the distortion of the particle double layer under the application of a DC electric field (Corni et al. 2008). However, numerous other theories (flocculation by particle accumulation, particle charge neutralization, electrochemical particle coagulation, electrical double layer distortion, and thinning mechanism) have been proposed to explain the particle interactions and the kinetics of deposition.

Several examples of membrane preparation using an EPD technique are reported. For example, EPD is used as a seeding method for making zeolite membranes (Abdollahi et al. 2007). Zeolites are crystalline structures which possess uniform and molecular-sized pores. Zeolite membranes have a great potential in separation and catalysis processes owing to their unique pore structures and adsorption properties and their high thermal, mechanical, and chemical stability compared with polymeric membranes. Since zeolites are negatively charged particles, they can be effectively attracted to the substrates of positive charge. By the aid of EPD, an oriented continuous layer of nano-sized zeolite seeds is formed on the support and acts as nuclei for the next step which is crystal growth under hydrothermal situation.

The EPD technique is also used for the preparation of membrane electrode assembly for fuel cell (Morikawa et al. 2004). A membrane

Electrophoretic Deposition,

Fig. 1 Schematic of electrophoretic deposition process. (a) Cathodic EPD and (b) anodic EPD



electrode assembly can be prepared by EPD process onto a Nafion membrane. A suspension consisting of ethanol, carbon powders with Pt catalyst, and Nafion polymer is used to obtain a stable dispersed solution. The thickness of the prepared catalyst layer is controlled by EPD duration or concentration of suspension. The cell obtained may present a higher electrochemical performance compared with ordinary cells.

Cross-References

- ▶ [Electrophoretic Painting](#)
- ▶ [Fuel Cell Membrane](#)
- ▶ [Zeolite Membrane](#)

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Electrophoretic Mobility

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When an electric field is applied across a given medium, charged solutes or particles suspended in the electrolyte are attracted toward the electrode of opposite charge. Viscous forces acting on the component tend to oppose this movement. When equilibrium is reached between these two opposing forces, the solutes or particles move with constant velocity. The velocity is dependent on

factors such as the strength of electric field or voltage gradient, the dielectric constant of the medium, the viscosity of the medium, and the zeta potential of the particles.

The electrophoretic mobility, μ (m^2/Vs), is the observed electrophoretic velocity, v (m/s), divided by electric field strength, E (V/m):

$$\mu = \frac{v}{E}$$

The electrophoretic velocity is the distance of migration divided by time, also called velocity of migration. Mobilities are sometimes expressed with a negative sign, because migration of the solutes or particles generally occurs in the direction opposite to the electrophoretic field (which is taken as reference).

The electrophoretic mobility of charged solutes, including proteins, is predicted using the Debye-Hückel-Henry theory (O'Connor et al. 1996). This theory is valid only for spherical nonconducting particles at low zeta potentials, with ions present in the electrical double layer behaving as point charges. The Debye-Hückel-Henry theory gives the mobility as

$$\mu = \frac{ze}{6\pi\eta r} \frac{f(\kappa r)}{(1 + \kappa r)}$$

where z is the net charge (dimensionless), e the elementary charge (C), r the particle radius (m), η the viscosity ($\text{kg m}^{-1} \text{s}^{-1}$), and $f(\kappa r)$ is the Henry correction factor, which has values between 1 and 1.5. The Debye-Hückel parameter, κ , is defined by

$$\kappa^2 = \frac{2e^2 N_A I}{\epsilon k T}$$

where N_A is the Avogadro's constant (kmol^{-1}), I is the ionic strength (kmol m^{-3}), ϵ is the permittivity ($\text{J}^{-1} \text{C}^2 \text{m}^{-1}$), k is the Boltzmann's constant (J K^{-1}), and T is the temperature. O'Brien and White (1978) obtained a more rigorous solution to the equations describing the electrophoretic mobility of a rigid spherical particle with a uniform charge density. The predictions of this model

coincide with those of the Debye-Hückel-Henry theory for systems with zeta potentials less than 25 mV.

The electrophoretic mobility of proteins has been determined through several microfiltration membranes under conditions of zero concentration driving force and with negligible adsorption on to the membranes occurring during the experiment (O'Connor et al. 1996). The initial mobility of both proteins is close to free-solution values at the same pH, after correction for the ionic strength of the buffer. This effect is explained by the effect of reduced free area in the membrane which is compensated by a corresponding increase in the potential gradient. Data were also obtained for mixtures of two proteins. Interactions occur when the two proteins are oppositely charged, changing the apparent mobilities from the free solution values.

Cross-References

- [Electrical Potential](#)
- [Electrophoresis](#)

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Electrophoretic Painting

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Electrophoretic painting, also called electrophoretic deposition of paint, electrodeposition painting, or E-coating, is an economical and corrosion-resistant technique for applying coatings to electrically conducting materials. It is widely used to

coat many industrial products such as automobile bodies and parts, tractors and heavy equipment, metal furniture, and beverage containers. The process is carried out with the use of anodes and cathodes in the painting tank. There are two types of electrophoretic painting: anaphoretic and cataphoretic painting. In anaphoretic painting the profiles will be the anode, and in cataphoretic painting the profiles will be the cathode. In the electrophoretic painting process, evolution of oxygen gas will take place at the anode, and hydrogen gas will be evolved at the cathode.

The electrophoretic paint is continuously circulated to avoid settling of the paint solids and heat resulting from the pumping process as well as from the passage of electric current. Dry coating thicknesses of the order of 20 μm are normally applied, using a voltage of 150–200 V for a time of 1–2 min. After painting, the profiles are rinsed before stowing at temperatures of 180–200 °C for 20–30 min. The electrophoretic paint may contain a water-soluble acrylic-based paint, the resin being rendered soluble by the addition of suitable amines such as melamine. When current is passed through the paint, the resin and pigments will migrate to the anode while the amine will be discharged at the cathode. During paint deposition the level of amine will increase, and this causes a decrease in paint deposition rate if allowed to continue. The most usual processes used for removal of excess amine are ultrafiltration often in combination with reverse osmosis.

After electrophoretic painting, ultrafiltration continuously treats the paint bath to produce permeate needed for rinsing metal parts (Agana et al. 2011). While permeate is used for rinsing, the mixture of paint and rinse water is returned to the paint bath from the downstream rinse system. The volume in the paint bath remains constant, and the process leads to a closed loop cycle including a multistage rinse system. No wastewater is produced and almost no deionized water is required for the purpose of rinsing. Different types of membranes are available for various types of paint. The type and size of the membrane modules are related to the needs of bath volume and characteristic parameters of the paint bath, such as total solids, pH, and temperature.

Cross-References

- ▶ [Electrophoretic Deposition](#)
- ▶ [Permeate](#)

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Electrospun Nanofiber Membrane for Biosensors

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A biosensor is an analytical device comprising three main elements: a biological recognition element able to interact specifically with a target, a transducer able to convert a change in property of the solution or surface into a recordable signal, and a processing system which is able to amplify and quantify the signal. The involved biomolecular interactions in the bio-receptor/analyte complex can be based on antibody-antigen interactions, enzymatic interactions, nucleic acid interactions, and cellular or analyte/synthetic receptor interactions.

Biosensors are generally classified according to transduction modes and recognition elements (D'Orazio 2003; Rodriguez-Mozaz et al. 2004) in five principal transducer classes that are electrochemical, optical, thermometric, piezoelectric, and magnetic. Moreover, electrochemical sensors may be subdivided into potentiometric, amperometric, or conductometric types (Thevenot et al. 2001). Biosensors represent nowadays the answer to a pressing need of advanced solutions for sensitive detection of the physiological chemicals involved in clinical diagnosis.

Within this scenario, electrospinning is an economic and versatile technology for producing one-dimensional nanomaterials that possess high specific surface area and high porosity. In this technology, an electrified jet of polymer solution is obtained by applying a relatively high electric tension. If the viscoelastic forces on the polymer solution are sufficient to contrast jet breaking, a nonwoven web of fibers ranging from few nanometers to several microns is collected on a proper support. Several reviews and books about electrospinning (Bhardwaj and Kundu 2010; Ramakrishna et al. 2005; Wendorff et al. 2012) are available for having a better understanding of this technique. The majority of electrospun fibers are polymer-based or polymer-inorganic composites. It has been shown they have a good biocompatibility and consequently they represent a good candidate for biosensor fabrication especially as a matrix for protein or enzyme immobilization (Li et al. 2014).

Among biosensors, monitoring changes in extracellular glucose concentration is one of the most important ones because it is related to both brain disease and neurological disorders, and it is also the key analyte for medical diagnostics and management of diabetes. A complete and exhaustive review on glucose biosensor and all the basic principles of them can be found in the scientific literature (Yoo and Lee 2010). The most common glucose biosensors achieve specific recognition of glucose by immobilization of the enzyme glucose oxidase (GOD) on the surface of electrodes Wu and Fan (2013). The basic concept of the glucose biosensor is based on the fact that the immobilized GOD catalyzes the oxidation of β -D-glucose by molecular oxygen, producing gluconic acid and hydrogen peroxide. Three general strategies are used for the electrochemical sensing of glucose: by measuring oxygen consumption, by measuring the amount of hydrogen peroxide produced by the enzyme reaction, or by using a diffusible or immobilized mediator to transfer the electrons from the GOD to the electrode (Yoo and Lee 2010). At this regard, polyvinyl alcohol (PVA) nanofibers have been shown to be useful in producing an amperometric glucose biosensor (Ren et al. 2006) which exhibited a rapid response time

(1 s) and a higher output current (μA level) to glucose in the normal and diabetic level. The linear concentration response range from 1 to 10 mM and the lower detection limit (0.05 mM) of the sensor can meet the demand in the detection of the glucose in medical diagnosis.

In enzyme-based biosensors, the sensitivity and longevity of the biorecognition element are functions of the physical design and the enzyme stability over time (Wilson and Gifford 2005). Moreover, temperature, pH, and other chemicals can easily affect the activity and stability of the immobilized enzyme as well as the immobilization chemistry and the microenvironment of the enzyme on the electrode (Marx et al. 2011).

In order to get an efficient enzyme encapsulation and the absence of interference from other coexisting electroactive species, the biocomposite based on Prussian blue, chitosan, and polyvinyl alcohol has been fabricated by electrodeposition and subsequent electrospinning in enzyme-friendly conditions. Prussian blue (PB), known as “artificial peroxidase,” has been employed in fabricating amperometric glucose biosensors because of its well-known capabilities for enhancing electron transport and excellent catalytic activity toward H_2O_2 reduction at a low overpotential. The modified electrode has been shown to exhibit such a rapid direct electron transfer rate that the glucose sensor exhibited excellent performance, which includes wider linearity, lower detection limit, and good stability in optimized conditions (Wu and Yin 2013).

Another way for improving sensitivity and lifetime of the immobilized enzyme is the application of conducting polymers to bioelectronic surfaces; the advantage of using such electrospun polymers is related to their ability to increase the signal-to-noise ratio (S/N), and, at the same time, they are a suitable matrix for the immobilization and entrapment of enzymes (Yang et al. 2014). For instance, Yang et al. compared the performance of enzyme-entrapped conducting polymer nanofibers (NFs) with reference to its conducting polymer film (F) counterpart. Among different conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has been chosen as support for GOD enzyme because of its

chemical stability and good electrical conductivity. Poly(L-lactide) (PLLA) has been electrospun on Pt microelectrodes followed by the electrochemical deposition of PEDOT-GOD on the Pt microelectrodes and around PLLA nanofibers. Comparing the performance of the two different nanostructured sensors (PEDOT-F vs. PEDOT-NFs), it has been shown that the increase of surface area related to the nanofibers affects both the impedance of the biosensor (which is sensitively lower) (Abidian et al. 2010) and it allows more GOD to be entrapped on the biosensor. Both of these results contribute to the increased sensitivity of the PEDOT-NFs-GOD biosensors.

Nevertheless, the scientific research on biosensors is moving also toward the design and development of nonenzymatic glucose sensors based on direct oxidation of glucose at modified electrode surface (Kong et al. 2012). According to Ding et al. (2010), metals (Au, Pt, Ni, Cu) and metal oxides (ZnO , CuO , etc.) have been exploited to construct a variety of enzyme-free glucose sensors. Among the aforementioned metal oxides, cobalt oxide nanofibers (Ding et al. 2010) have been obtained by electrospinning and subsequent calcination, and they have been used for glucose detection in an alkaline medium. The developed sensor has been shown to have a fast response time (less than 7 s), a high sensitivity of $36.25 \mu\text{A mM}^{-1}\text{cm}^{-2}$, good reproducibility and selectivity, and a detection limit of $0.97 \mu\text{M}$ ($\text{S/N} = 3$). The high sensitivity and low detection limit has been hypothesized to be related to the excellent catalytic property of the as-prepared Co_3O_4 nanofibers and to their highly porous 3D network. The latter provides high specific surface area and numerous active sites, and it allows the access of analytes to the active catalytic sites with minimal diffusion resistance. Another attempt to get nonenzymatic glucose sensor has been reported in the research of Cao et al. (2011), wherein nickel oxide microfibers (NiO-MFs) have been directly immobilized onto the surface of fluorine tin oxide (FTO) electrode by electrospinning followed by calcination without using any immobilization matrix. The amperometric performance of glucose at

NiO-MFs-modified electrode have shown an ultrasensitive current ($1785.41 \mu\text{A mM}^{-1} \text{cm}^{-2}$) response and low detection limit of $3.3 \times 10^{-8} \text{M}$ ($\text{S/N} = 3$).

Despite the presence of enzyme-based and nonenzyme-based biosensors, there are also other support-enzyme hybrid substrate materials for biosensors. An example that has been investigated by researchers was based on water-stable PVA and PVA/poly(ethyleneimine) (PEI) nanofibers decorated with silver nanoparticles (AgNPs) (Zhu et al. 2013). By combining an in situ reduction approach and electrospinning technique, a H_2O_2 , glutathione (GSH), and glucose detection biosensor has been obtained, showing a high sensitive detection of H_2O_2 with a detection limit of $5 \mu\text{M}$ and a fast response, broad linear range, low detection limit, and excellent stability and reusability.

Looking at the aforementioned literature, it appears evident that the ongoing trend in biosensor fabrication is the use of specific nanomaterials to get better sensitivity, lower detection limit, and linear response range. Further evidence of this is the H_2O_2 -modified electrode based on hemoglobin (Hb) collagen and carbon nanotubes (CNTs) proposed by Li et al. (2014). Hb has been used because of its similar structure to peroxidase, CNTs for the electrical properties, and collagen for its excellent biocompatibility. Therefore, the resulting hemoglobin-collagen-carbon nanotube (Hb-collagen-CNT) composite nanofiber-modified electrode has excellent performance, thanks to the great surface area and the high porosity of the three-dimensional reticular structure which ensures more channels for both electron transfer and diffusion of H_2O_2 .

Among enzymes currently used in biosensor fabrication, urease (Sawicka et al. 2005), fructose dehydrogenase (Marx et al. 2011), α -chymotrypsin (a proteolytic enzyme acting in the digestive systems of many organisms) (Jia et al. 2002), and lipase (Li et al. 2007; Ye et al. 2006) represent just a few examples of the ongoing research. The large surface area of electrospun nanofibers has been found to be important for increasing both the amount of immobilized enzymes and their own catalyzing

activity, thanks to an effective reduction of the diffusion resistance of the substrates/products.

Further challenge in detecting DNA repair represents a key factor in cancer diagnostic. Due to the subtlety of DNA damage, it is difficult to sense the presence of damaged repair with high selectivity and sensitivity. In this regard immobilizing DNA on gold/polymeric electrospun nanofibers and their use in electrochemical sensing of DNA repair processes have been shown to be very promising, showing the potential of these low-cost devices for sensing applications (McWilliams et al. 2014). Polyacrylonitrile electrospun fibers coated with gold nanoparticles have been tested and thiolated DNA has been assembled on these fibers. It has been demonstrated that the fibers themselves become the working electrode of the sensors, modified with either the lesion-bearing or defect-free DNA monolayers. From the reported assays, the device sensitivity has been found to be on the order of femtomoles per electrode, and it means that sensing can be accomplished with even 1 ng of enzyme.

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Electrospun Nanofibers for Water and Wastewater Treatment Applications

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Water pollution is the contamination of water bodies (e.g., lakes, rivers, oceans, aquifers, and groundwater), and it occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. Direct sources include effluent outfalls from factories, refineries, waste treatment plants, etc., that emit fluids of varying quality directly into urban water supplies. Indirect sources include contaminants that enter the water supply from soils/groundwater systems and from the atmosphere via rainwater. Soils and groundwaters contain the residue of human agricultural practices (fertilizers, pesticides, etc.) and improperly disposed of industrial wastes. Atmospheric contaminants are also derived from human practices (such as gaseous emissions from automobiles, factories, and even bakeries). Contaminants can be broadly classified into organic, inorganic, radioactive, and acid/base. Moreover, bacteria and virus represent a dangerous class of contaminating agents, which are responsible of diseases in developing countries.

Microbial Control of Water

Currently the basic water treatments for microbial control require chemical disinfectants and membrane-based filtration systems. If the formation of harmful disinfection by-products from chemical disinfectants is the potential drawback that makes their use not completely reliable (Li et al. 2008), water filtration membrane is affected by biofouling and virus penetration. Biofouling can be considered as a biotic form of

organic fouling, and it represents a major problem in nanofiltration (NF) and reverse osmosis (RO) membrane filtration.

At this regard, electrospun nanofibers have been found to be a good candidate for improving the performance of filtering media. Antifouling properties can be achieved by plasma treatment or surface graft polymerization of nanofibers, as suggested by the literature (Musale and Kumar 2000). Another advantage related to the use of electrospun nanofibers for microbial control is the capability to get a wide range of assemblies, for instance, antimicrobial nanofibers themselves and nanobiocides, which include metal, metal-oxide nanoparticles, engineered nanomaterials (fullerenes and carbon nanotubes), and natural substances (Botes and Cloete 2010). For instance, nanoparticles of Ag, TiO₂, and ZnO represent low-cost materials with a well-known antimicrobial activity that can be properly attached to nanofibers reducing potential toxicity and leaching effects.

Polyurethane, poly(vinylidene) fluoride-co-hexafluoro-propylene (PVDF-HFP), and polycarbonate with quaternary ammonium salt are just few examples of antimicrobial nanofilters which have been shown to have a very good filtration efficiency of 0.3 mm size particles (99.93 %) and a very strong antimicrobial activities against both *S. aureus* and *E. coli* (Yao et al. 2008, 2009; Kim et al. 2007).

Desalination

Another challenging task related to the water issue regards the need of alternative sources in order to tackle the higher demand for fresh water and energy resources. Desalination technology that converts seawater into clean water has been found to be a suitable approach for it. Among the different membrane separation processes, membrane distillation (MD), electrodialysis (ED), reverse osmosis (RO), freeze desalination (FD), ion exchange (IX), and nanofiltration (NF) have been developed as desalination technologies (Sundarrajan and Ramakrishna 2013).

Nanofiltration is a type of pressure-driven membrane process with properties in between reverse osmosis (RO) and ultrafiltration (UF), which has been found to be adequate for desalination with low salt content. According to the established technology, in order to reduce the resistance and enhance the flux, thin film composite membranes (TFC) are commonly used. They are based on three layer, that is, a nonwoven fabric as support, a middle porous support, and a top layer which is responsible for the selective salt removal. Within this scenario, electrospun nanofibers can be used as a mid-layer membrane in order to achieve higher flux and low fouling behavior than the commercial NF membranes (Yung et al. 2010). Nevertheless, the applicability of electrospun membranes as self-supporting NF membranes has been proved (Kaur et al. 2012) even though a careful optimization of the whole system needs further studies in terms of process optimization and cost analysis.

As regards desalination by membrane distillation (MD), nanofibrous membranes based on electrospun polymers (polyvinylidene fluoride, PVDF) and copolymers (PVDF-co-F6PP, PVDF-co-hexafluoropropene) have been proven to reduce the energy requirements of direct contact membrane distillation process, thanks to the higher permeate flows (Khayat et al. 2011; Shih 2011) than PTFE commercial membranes. Very good performance in a direct contact membrane distillation setup could be achieved also by self-supporting carbon nanotube (CNT) membranes (Dumée et al. 2011), which have to be properly modified for enhancing their hydrophobicity and that allow to get a 99 % salt rejection and a flux rate of 12 kg/m².

Heavy Metal Ions Removal

Water pollution by heavy metal ions is another important related issue because long-term exposure to metal ions such as lead (Pb) can result in acute or chronic damage to the brain and the central nervous system on humans. Furthermore, heavy metals are dangerous because they tend to

bioaccumulate, i.e., the concentration of a chemical increases in a biological organism over time, compared to the chemical's concentration in the environment (Lee et al. 2013). Among the technologies employed for the treatment of contaminated water (chemical oxidation, precipitation, IE, RO), adsorption and membrane separation could be enhanced by electrospun nanofibers. In the literature several examples are reported, the central ideas of which are:

- i. The functionalization of the fibers with such molecules able to bind metal ions
- ii. The surface modification of polymer in order to vary certain properties, such as hydrophilicity or hydrophobicity, water absorbency, adsorption capacity, and resistance to microbial attack
- iii. The production of mixed nanocomposite fibers

As regards the functionalization of fibers (point i), rhodanine is a heterocyclic molecule that belongs to the sulfur-containing N and O organic compounds which possesses uptake performance toward Ag (I), Pb (II), and Hg (II) ions (Lee et al. 2013). On the other hand cellulose and chitosan-/polyacrylamide-modified nanofibers have been proven to be suitable for the adsorption of trace of metals (Cd, Pb, Cu, Cr, and Ni) from the river water and treated water (Musyoka et al. 2013). Their adsorption capacity has been enhanced (point ii) by surface modification using furan-2,5-dione. The electrospun iron oxide–alumina fiber systems represent an example of nanocomposite fibers (point iii) that have been used as adsorbent for the removal of heavy metal ions, i.e., Cu^{2+} , Ni^{2+} , Pb^{2+} , and Hg^{2+} from aqueous system (Mahapatra et al. 2013).

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Electrospun Nanofibrous Membranes

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Introduction

Nanofibers are an interesting and versatile class of one-dimensional (1-D) nanomaterials, with diameters ranging from tenths to hundreds of nanometers, which have been recognized as promising due to their outstanding properties in terms of high porosity, excellent pore interconnectivity, small diameters, and high surface-to-volume ratio. Among the different nanofiber manufacturing technologies, electrostatic spinning or *electrospinning* represents the easiest, most promising, and versatile method for the generation of aligned or randomly distributed nanofibers of a rich variety of different materials like synthetic and natural polymers (Huang et al. 2003), composites (Sahay et al. 2012), ceramics (Dai et al. 2011), and metals (Wu et al. 2007).

With this technique that is essentially a variation of the electrostatic spray (or *electrospraying*), a fiber is produced thanks to the solidification of an electrified jet of a solution that is stretched by the repulsive action of surface charges and evaporation of solvent. The main difference with respect to *electrospraying* is the presence of high elongational viscous forces generated by the chain entanglements of the polymer present in the solution that, thanks to the application of a strong electric field, prevent the formation of liquid droplets in favor of a rapid whipping jet. The electrospun solution is essentially polymer based, with the possibility to add metal or ceramic precursors that after *electrospinning* treatments can generate the corresponding nanofibers.

An extensive research activity has been carried in the last years toward the evaluation of electrospun nanofibrous membranes (ENMs) in the context of membrane technology, fueled by

the advantages offered in terms of cost and productivity over more complicated bottom-up approaches, flexibility of the membranes, and the potential upscaling for industrial production (Persano et al. 2013).

Fundamentals

The generation of nanofibers by *electrospinning* starts from a solution of a proper solvent in which the desired material is dissolved at a suitable concentration. This solution is usually poured in a syringe or a pipette from which it is let flown through a nozzle using a micropump, and by means of a high-voltage direct current power supply (5–50 kV), an electrostatic field is applied between the nozzle and a metal collector with opposite polarity. By increasing the intensity of the electric field, a charge is induced on the surface of the solution at the tip of the capillary. The mutual repulsion of the charges elongates the hemispherical drop to form a conical shape (*Taylor cone*). Once that the electric field has reached a threshold value, the electrostatic force overcomes the surface tension and a charged jet of solution is ejected from the tip of the Taylor cone, producing a jet that travels toward the metal collector. During this last phase the jet undergoes a whipping process in which it is stretched and the solvent of the solution evaporates leaving a fiber that is collected on a grounded collector.

The morphology and diameter of electrospun nanofibers depend on a wide range of parameters, which can be classified according to three main different categories:

- *Solution parameters*: type of solvent, viscosity, molecular weight and molecular weight distribution, vapor pressure, surface tension, and solution conductivity
- *Process parameters*: solution feeding rate, electric field strength, distance between the tip and the collector, needle diameter, composition, geometry, and motion of the collector
- *Ambient parameters*: temperature, humidity, and air velocity.

Between them viscosity has a prominent role in relation to the morphology of the nanofibers. For polymer solutions of low viscosity, surface tension is the dominant aspect and just beads or beaded nanofibers are obtained. As the viscosity of the solution is increased, the beads become bigger, the average distance between them longer, and the shape of the beads changes from spherical to spindle-like with a decrease of the fiber diameter. At a suitable concentration, smooth nanofibers without defects can be obtained, but with a progressive increment of its value, the fibers increase their diameter until they change their shape into micro-ribbons. Usually the proper viscosity is defined in relation to the specific polymer-solvent system, and for a given polymer-solvent system, it can change according to the molecular weight of the polymer. Complex architectures like core-shell, porous, and hollow structures can be formed by *electrospinning* through the incorporation of nanoparticles into fibers, *co-electrospinning* of different polymers, or employing solutions with different boiling point solvents, while modification of the electrode-collector system allows to orientate the fibers and to obtain 3-D structures (Teo et al. 2011).

Electrospun nanofibers can also be obtained from polymer melts at high temperature, from a combination of a magnetic and electric field, aerated polymer solution, and from multi-jet devices in order to improve production rate.

Applications

The interesting properties related to the possibility of obtaining nanometric fibers from *electrospinning* allow their use for several potential applications, with a multidisciplinary perspective. Broadly speaking it is possible to identify four main areas of interest (Ramakrishna et al. 2005): bioengineering, environmental engineering and biotechnologies, energy and electronics, and, finally, defense and security. In this framework the specific fields of applications in which electrospun nanofibers are directly in contact with membrane technology are several,

including the most traditional and advanced technologies: air and water filtration, fuel cell membranes and battery membrane separators, biomedical applications, and many others. Most of these applications haven't already reached their industrial level, but the promising results from the research field and their different potential applications are believed to encounter the interest of industry and governments. Actually the most industrially developed products based on ENMs are filters for air purification. Potential products ready to market are related to liquid filtration and energy storage, in the short-medium period, and to the biomedical field, in the medium-long period (Persano et al. 2013).

Air and Water Filtration

ENMs' high specific surface, porosity and permeability, tailorable thickness, and fiber diameters are desirable features for filtration applications. These materials have been employed for several years for air filtration and recently, at a research level, even for microfiltration, ultrafiltration, and nanofiltration in the field of water treatment. The advantages of electrospun nanofibers compared to conventional air filter media are related to a higher filtration efficiency, lower pressure drops, and energy savings. Indeed, nanofibers with diameters lower than 0.5 μm have much higher capability to collect fine particles because of the slip flow that increases diffusion, interception, and inertial impaction efficiencies, determining a lower drag force around the fibers and, thus, lower pressure drops. In addition these media are easy to clean, enabling them to significantly extend the life of filters and reducing the maintenance costs. Their potentials have shown possible applications in air filtering media (Barhate and Ramakrishna 2007), especially for high-efficiency particulate and low-penetration air filters, filters for transportation applications, adsorptive catalytic gas filter for respirators, filter media for pulse clean cartridges in dust collection, and cigarette filters for smoke filtration.

ENMs can be employed also for water treatment (Cloete et al. 2013) and generally show high flux rate and low transmembrane pressure with performance comparable to those commercially

available. The main interesting application in this area is related to desalination, VOC gas stripping, oil/water emulsion separation, microbial, organic compounds, and heavy metal removal. However, for solid-liquid filtration, very high surface-to-volume ratios promote membrane fouling. For this reason and for improving membrane performances, ENMs can be surface modified (Nasreen et al. 2013), in order to add functional groups or functionality, with processes like in situ graft and interfacial polymerization, plasma treatment, wet treatment, coating, and blending with surface-modifying agents. A main drawback for the employment of electrospun nanofibers for such applications is their mechanical strength which is not sufficient to withstand macroscopic impact during filtration application such as normal liquid or air flows passing through them. Hence, they need to be used as active coating layer on existing melt-blown supportive fibrous media (composite membrane) or the fibers need to be bonded to enhance mechanical properties.

Fuel Cell and Battery Separator Membranes

Another area in which ENMs can have promising applications is that of energy-related applications and devices (Cavaliere et al. 2011), especially for polymer fuel cell and lithium-ion battery electrolyte membranes.

Research efforts on polymeric proton exchange membranes for fuel cells have led the interest of researchers toward the employment of ENMs as porous reinforcing mats to minimize in-plane swelling and shrinking. Nanofibers are also able to increase proton conductivity with respect to bulk film, thanks to their highly oriented ionic domains (Dong et al. 2010) and provide good mechanical strength, while the remarkable flexibility of their production process allows to adequately tailor their final morphology for composite membranes. Fuel cell membranes are semi-permeable membranes that have the function to be proton conductive, electron insulating, and dense in order to avoid fuel crossover. For this reason two types of approaches can be used when employing *electrospinning* for such application. The first is related to the *electrospinning* of

nonconductive or less conductive polymer into a porous matrix, which acts as mechanical reinforcement when the pores are filled with a highly proton-conductive component. Alternatively, a highly proton-conducting matrix is electrospun into a porous fiber mat and subsequently reinforced with a secondary polymer to provide mechanical stability. The proton-conductive polymers are usually chosen between perfluoro-sulfonic acid and sulfonated polymers that can be coupled with organic or inorganic particles as conductor enhancers or to improve strength and hydrophilicity.

Electrospun mats are also attractive alternatives to polymer gel electrolytes for lithium-ion batteries, since they can be employed as matrix in which the electrolyte can be encapsulated improving ionic conduction across the membrane and mechanical strength while providing good water uptake. In these fields the most widely studied polymer has been poly(vinylidene fluoride) (PVDF) thanks to its good electrochemical and thermal stability. However, PVDF-based gel polymer electrolyte with its high crystallinity limits the ion migration, lowering the battery performance. ENMs with their porous membrane are capable to overcome this problem, and PVDF and other alternative polymers and blend have been explored by *electrospinning* with encouraging results.

Biomedical Applications

Nanofiber research applications in the biomedical field have a multifaceted perspective spreading between tissue engineering, drug delivery, and wound dressing (Agarwal et al. 2008). Tissue engineering is an emerging multidisciplinary area in which nanofibers represent an important advancing front for the production of suitable scaffolds of different materials that can mimic natural extracellular matrix. To this purpose ENMs have been tested as natural, synthetic, and composite scaffolds for different types of targeted tissue including blood vessel, cartilage, bone, nerve, and many others. The small diameter of the fibers and their high surface area are beneficial for cell attachment and bioactive factor loading, enhancing cell growth.

Drug delivery membranes incorporate a drug component that can be patched on wound of surgery or encapsulated into pharmaceutical capsules to deliver the drug through the digestive system of the patient. Polymeric electrospun drug delivery systems are advantageous for such task because they can deliver drugs efficiently to a localized area, with the possibility to vary the release rate by simply varying the fiber diameter or the loading dosage. The possibility of choosing different materials, processes, and processing conditions allows to reach the desired encapsulation efficiency, preserving bioactivity (Zamani et al. 2013). Several drugs have been incorporated successfully into electrospun media obtaining better performance over normal cast film and with the possibility to load insoluble drug for enhancing their dissolution.

ENMs have also exhibited potential in wound dressing thanks to the possibility to generate homogeneous scaffolds, provide uniform adherence, and wet wound surface without fluid accumulation. They can provide high gas permeation and protection from infection and dehydration, extending their applications on different types of wounds as compared to traditional wound dressing materials and opening new doors for the next generation of wound dressing materials.

Other Applications

Electrospun materials from stable polymers or ceramic fibers are also ideal candidates as supports for homogeneous and heterogeneous catalysis in gas phase, since they can provide high surface area and high porosity. The catalyst, which is usually a semiconductor, can be the nanofibrous mat itself, or it can be subsequently added by surface modifications or deposition. Examples are organic or inorganic nanofibers on which metals or semiconductor nanoparticles are deposited or embedded for catalytic (Basheer 2013) and photocatalytic oxidation (Modesti et al. 2014) and synthesis (Formo et al. 2009) of organic compounds in gas phase. The advantages of the high surface areas of the catalytic filters obtainable with this technique are related to higher activity with respect to common porous

catalysts for the abatement of selected compounds.

The characteristics of ENMs match well the requirements for different types of sensing devices (Ding et al. 2009) including acoustic wave, resistive, gravimetric, photoelectric, optical, and amperometric sensors. Indeed, ENMs' high surface area has the potential to provide unusually high sensitivity, fast response time, and lower detecting limits. In this case different approaches can be employed to provide a sensing capability to nanofibers, such as *electrospinning* of a polymeric sensing material, incorporation of sensing molecules into nanofibers, or application of sensing material on nanofiber surface via coating/grafting technique, employing organic and inorganic polymer.

Other potential applications of ENMs include affinity membranes for protein purification (Ma et al. 2005) and protective clothing against nanoparticles (Faccini et al. 2012) on textile support.

Cross-References

- [Nanofiber](#)
- [Oil-Water Emulsion](#)
- [Proton-Exchange Membranes for Fuel Cells](#)
- [Ultrafiltration \(UF\)](#)

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Further Readings

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Electrospun Polyethersulfone Nanofiber Membranes

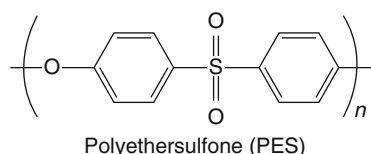
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Electrospun polyethersulfone (PES) nanofiber membranes are semipermeable membranes obtained by *electrospinning* that have been explored for possible applications concerning water filtration (*microfiltration*, *nanofiltration*, and *engineered osmosis*), composite polymer electrolyte membranes, and tissue engineering.

Polyethersulfone (PES) is a high-performance aromatic polymer which belongs to the family of polysulfones. The basic repeating unit of the polymer backbone consists of *para*-linked aromatic groups connected by ether and sulfone groups (see Fig. 1).

PES is synthesized by polycondensation of 4,4-sulfonylbisphenol (bisphenol S) with



Polyethersulfone (PES)

Electrospun Polyethersulfone Nanofiber Membranes, Fig. 1 Repetitive unit of polyethersulfone

4,4'-dichlorophenyl sulfone via nucleophilic substitution at high-reaction temperature (up to 285 °C) in the presence of a suitable solvent like diphenyl sulfone, sulfolane, or N-methyl-2-pyrrolidone (Parker et al. 2012).

PES is a widely employed polymer for membrane fabrication due to its interesting properties in terms of high glass transition temperatures, good mechanical strength and stiffness, and outstanding thermal and oxidative resistance. This polymer can be electrospun from solutions of suitable concentration with polar aprotic solvents (e.g., dimethylacetamide) in order to produce nanofibers with average diameters of 0.75–2 μm and average specific surface area of 15–30 m^2/g , by changing the process parameters (Kwak et al. 2013).

Electrospun nanofibrous membranes (ENMs) are a new class of energy-saving membranes that are under extensive study because of their high interconnected porosity and tunable pore size that can give high permeability and selectivity. One of the most important fields of interest for ENMs is water filtration for which these membranes could overcome some intrinsic limitations of conventional porous polymeric membranes. However ENMs suffer of poor mechanical strength, while PES, even if extensively used for commercial membranes, is a highly hydrophobic polymer so the synthesis of composite membranes is the usual approach to solve these issues. PES ENMs can be employed for dye and heavy metal removal by blending with polymers that incorporate functional groups that have binding/chelating capability (Min et al. 2012; Wu et al. 2014). The mechanical properties of these membranes can be improved by interfiber adhesion/junction (Yoon et al. 2009; Homaeigohar et al. 2012), while the hydrophilicity can be increased by oxidation treatment (Yoon et al. 2009). A combination of both improvements can be achieved by incorporation of hydrophilic inorganic particles which can also allow a higher thermal stability (Homaeigohar et al. 2011). PES ENMs can be employed even as a middle layer in thin film composite polymeric membranes for engineered osmosis with the advantage to provide higher osmotic fluxes than their commercial counterparts (Bui et al. 2011).

Other potential applications concern polymeric scaffolds as substrate for stem cell culture made of pristine (Christopherson et al. 2009; Ardeshirylajimi et al. 2013) and modified (Chua et al. 2006; Shabani 2009) PES, for which both the fiber diameter and the type of functionalization can have a prominent role in the infiltration, differentiation, and proliferation of the cells.

The high stability of the polymer and its chain flexibility due its structure make PES a suitable candidate as non-fluorinated replacement for proton exchange membranes, especially for direct methanol fuel cells. By sulfonation it is possible to introduce proton conducting functional groups along the polymer chain, while by electrospinning a suitable nanofibrous web can be produced. This nonwoven structure can be filled with Nafion to obtain a compact membrane with higher electrochemical performances with respect to Nafion 112 and Nafion 117 dense membranes (Shabani et al. 2010; Hasani-Sadrabadi et al. 2011).

Cross-References

- [Electrospun Nanofibrous Membranes](#)
- [Proton-Exchange Membranes for Fuel Cells](#)
- [Ultrafiltration \(UF\)](#)

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- fertilization and contains from 64 to several hundred cells organized in an outer shell, the trophectoderm, and the inner cell mass (ICM). The ICM is the locus of pluripotent cells destined to yield all the tissues of the developed organism. In the process of obtaining embryonic stem cells, the trophectoderm is removed by immunosurgery, and the ICM is disaggregated and plated on feeder cells. Ethical issues surround the derivation of human ES cells from in vitro fertilized blastocysts.
- Embryonic stem cells have pluripotency and indefinite replication characteristics. These cells have the capacity to give rise to differentiated progeny representative of all three embryonic germ layers (ectoderm, endoderm, and mesoderm). ES cells are able to differentiate in all cell types differently from adult stem cells that can produce only a limited number of cell types. It is possible to modulate the differentiation of stem cells in a given phenotype by using specific growth factors and molecules, which trigger the differentiation process.
- ES cells for their ability of propagating themselves indefinitely represent a valuable tool for both research and regenerative medicine. They can serve as an unlimited source of any cell type in the body; human ES cells could yield highly effective in vitro models for use in drug discovery programs and provide a renewable source of cells for use in transplantation therapy. Cell therapies based on the use of ES cells have been proposed for tissue replacement after injury or disease.
- Adult stem cells, isolatable from bone marrow, adipose tissue, tooth pulp, and many other locations of the body, are capable of self-renewal and can be readily expanded ex vivo for several passages without losing their self-renewal capacity. Mesenchymal stem cells can differentiate into multiple tissue-forming cell lineages such as osteoblasts, chondrocytes, adipocytes, tenocytes, and myocytes. Recent work on the differentiation of bone marrow-derived mesenchymal stem cells into neuron-like cells is another demonstration of considerable plasticity of adult mesenchymal stem cells. Stem cells are often a preferred cell source for regeneration of multiple cell lineage tissues. The ability to expand stem cells is desired to generate cells for tissue engineering in clinical and pharmaceutical applications (Rahaman and

Embryonic Stem (ES) Cell

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Embryonic stem (ES) cell is a totipotent stem cell derived from an early stage embryo, which is called blastocyst. This stage is reached 4–5 days after

Mao 2005). Conventional methods for expanding stem cells or progenitor cells comprised polystyrene culture dishes and component of extracellular matrix such as collagen. Alternatively biocompatible and biodegradable materials have been proposed to support cells and promote their differentiation and proliferation toward the formation of a tissue (Piscioneri et al. 2011).

Advances in cell-based therapies would not have been possible without the innovative design and fabrication of several generations of biomaterials. Novel biomaterials with distinct properties are necessary to accommodate the growth and interactions of multiple cell lineages in composite tissue constructs (Griffith 2000). Membrane systems provide the temporary structural framework for tissue-forming cells to synthesize extracellular matrices and other functional components in the intended shape and dimensions (De Bartolo and Bader 2013). They can respond on the key demands for utilizing cell-based therapies to engineer composite tissue constructs with a purposeful orientation toward anatomic structures that the tissue-engineered constructs are intended to regenerate. Development of new intelligent biomaterials in synergy with cell biology will advance stem cell-based clinical therapeutics. Engineered membranes have the potential to mimic and control the physical, chemical, and biological factors necessary for guiding stem cell differentiation (Pavlica et al. 2009). They are currently being investigated to act as scaffolds to guide and improve 3D tissue formation, substrates to enhance cell culturing techniques, vehicles for cell delivery, and sources of immobilized and/or time-released factors. They can be applied to the regeneration of numerous tissue types, including the liver, pancreas, bone, cartilage, skin, and nerves, and are being used for the in vitro realization of physiological models.

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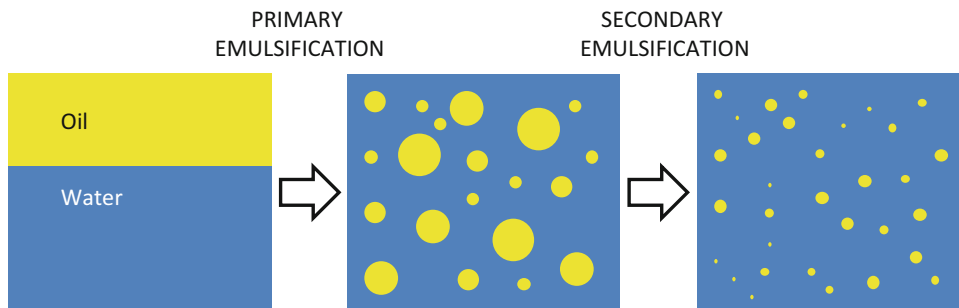
Emulsification

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Emulsification is a process by which one phase is broken up, dispersed, and distributed in a second immiscible or partially miscible phase (Leal-Calderon et al. 2007). Many different emulsification methods can be identified, and they can be distinguished in nonmechanical and mechanical methods. The nonmechanical methods include the dispersed phase precipitation and the phase inversion. Changes in the phase behavior of the substances to be emulsified, promoted by variation of temperature or composition or by mechanical stress, are used to achieve the desirable state of the system. The mechanical methods of producing emulsions include the use of high-speed mixers, colloid mills, high-pressure valve homogenizers, ultrasonic homogenizers, microfluidization, and membrane emulsification. Depending on the nature of the starting materials, emulsification can be distinguished into two categories. The creation of an emulsion directly from two separate liquids is defined as primary emulsification, whereas the reduction in size of the droplets in preformed emulsion is defined as secondary emulsification (Fig. 1).

The physical processes that occur during emulsification can be highlighted by considering the behavior of two immiscible liquids in a container such as oil and water. Their thermodynamically



Emulsification, Fig. 1 Emulsification

most stable state consists of a layer of oil on top of a layer of water that allows to minimize the contact area between the two phases. To create and emulsion, it is necessary to supply energy in order to disrupt and mix the oil and water which is usually achieved by mechanical agitation. The droplets formed are constantly moving around and frequently collide and coalesce with neighboring droplets. The presence of an emulsifier prevents the merging together of the droplets after they are formed. The emulsifier adsorbs to the surface of the droplets during emulsification and forms a protective membrane that prevents the droplets from coming close enough together to coalesce. The rates of droplet disruption, droplet coalescence, and emulsifier adsorption within a particular homogenizer depend on the flow profile that the fluids experience: (i) laminar flow which is a regular, smooth, and well-defined flow with relatively low flow rate; (ii) turbulent flow which is an irregular, chaotic, and ill-defined flow with relatively high flow rate characterized by the formation of eddies within the fluid; and (iii) cavitation flow which is an extremely complex flow because of the formation of small cavities that implode and generate shock waves. The tendency for one flow regime is a consequence of the balance of viscous and inertial forces acting on the fluid expressed by the Reynolds number:

$$Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{L v \rho_c}{\eta_c}$$

where L is some characteristic length of the system, v is the average fluid flow velocity, ρ_c is the density of the fluid, and η_c is the viscosity of the

fluid. When the viscous forces generated within a fluid dominate the inertial forces (low Re), the flow profile is laminar; when the inertial forces dominate (high Re) in the flow profile, it is turbulent. The size of the droplets produced by a homogenizer depends on a balance between the two opposing physical processes: droplet disruption and droplet coalescence. The interfacial forces that tend to hold the droplets together and the disruptive forces generated within the homogenizer that tend to pull the droplets apart are involved in droplet disruption process. To deform and disrupt a droplet during homogenization, it is necessary to apply an external force that is significantly larger than the interfacial force. The interfacial force is described by the Laplace equation:

$$\Delta P = \frac{4\gamma}{d}$$

where γ is the interfacial tension between the two liquids, d is the droplet diameter, and ΔP is the Laplace pressure which acts across the interface toward the center of the droplet. The equation indicates that the pressure required to disrupt a droplet increases as the interfacial tension increases or as the droplet size decreases. For a droplet to be broken up during homogenization, the disruptive forces must exceed the interfacial forces and their duration must be longer than the time required for droplet deformation. The relative magnitude of disruptive and interfacial forces is characterized by the Weber number (We):

$$We = \frac{\text{disruptive forces}}{\text{interfacial forces}}$$

Emulsification, Table 1 The type of homogenizers used for emulsification

Homogenizer type	Droplet formation mechanism	Productivity	Droplet size and size distribution	Energy density (J m^{-3})
High-speed mixer	Droplets break up in TI, TV, and LV flow regime	Batch or continuous	$>2 \mu\text{m}$, polydisperse	Low-high
Colloid mill	Droplets break up in LV and TV flow regime	Continuous	$>1 \mu\text{m}$, polydisperse	Low-high $10^3\text{--}10^8$
High-pressure homogenizer	Droplets break up in TI, TV, LV, and CI flow regime	Batch or continuous	$>0.1 \mu\text{m}$, polydisperse	Medium-high $10^6\text{--}10^8$
Ultrasonic	Droplets break up in CI flow regime	Continuous	$>0.1 \mu\text{m}$, polydisperse	Medium-high $10^6\text{--}10^8$
Microfluidization	Droplets break up in TI and TV flow regime	Batch or continuous	$<0.1 \mu\text{m}$, polydisperse	Medium-high 10^6 to 2×10^8
Membrane	Droplet detachment by wall shear stress	Continuous	$>0.3 \mu\text{m}$, narrow	Low-medium $<10^3\text{--}10^8$

TI turbulent inertial, TV turbulent viscous, LV laminar viscous, CI cavitational

During homogenization droplet-droplet collisions are particularly rapid because of the intense mechanical agitation of the emulsion. Droplet coalescence will depend on the time taken for the emulsifier to be adsorbed to the surface of the droplets relative to the time between droplet-droplet collisions. The flow profile and the nature of the emulsifier used influenced these times.

The characteristics of the different type of homogenizers are reported in Table 1.

High-speed mixer and colloid mills are suitable for preparing emulsions with relatively large droplet sizes ($>1 \mu\text{m}$), while the other types of homogenizers can be used to prepare submicron droplets. High-speed mixers, ultrasonic homogenizers, microfluidizer, and membrane homogenizers can be used for primary emulsification, whereas high-pressure valve homogenizers and colloid mills are most suitable for secondary emulsification. Most of these homogenizers have high productivity and they are able to work in a batch or continuous operation mode. In particular, membrane homogenizers have appreciably lower productivity than the other major types of homogenizers. The use of membrane homogenizers may be particularly useful where narrow droplet size distributions are important such as for drug delivery.

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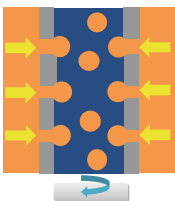
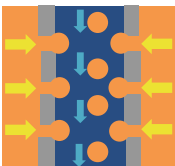
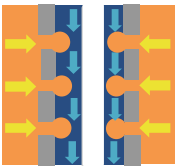
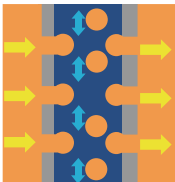
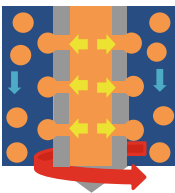
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Emulsification by Membrane Operations

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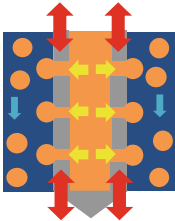
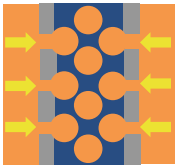
Emulsions can be generated using membrane operations by: (i) *direct membrane emulsification*, where a microporous membrane is used to disperse one of two immiscible liquids as a form of droplets into another liquid or by (ii) *premix membrane emulsification*, where a coarse emulsion is extruded through the membrane pores in order to generate fine droplet emulsion. A pressure is required to cause the dispersed phase to permeate through the membrane. If any shear is applied on the membrane surface, droplets can be spontaneously detached from the pore outlets on the action of the interfacial tension when they reach a certain size. The method is referred as *static membrane emulsification* (Kukizaki 2009). The shear on the membrane surface can be generated by moving the continuous phase or using moving membranes. The method is referred as *dynamic membrane emulsification*. The shear stress is generated by the continuous phase flowing tangentially to the membrane surface (*cross-flow membrane emulsification*) (Williams et al. 1998) or stirred

Emulsification by Membrane Operations, Table 1 Different membrane operations used for the production emulsion droplets

	Advantages	Disadvantages
Dynamic membrane emulsification		
Stirred ME 	Suitable for low volumes of continuous phase Useful to study the effect of different experimental conditions on the emulsion preparation	Emulsion production at batch scale The shear stress at the membrane surface is nonuniform and depends on the cell geometry
Cross-flow ME 	Constant shear stress at the membrane surface Suitable for large-scale production and continuous or semicontinuous operation	Emulsion droplet breakup as a consequence of the recirculation High dispersed phase concentration is obtained after a long time of operation
Cross-flow ME with static promoter 	Constant shear stress at the membrane surface Suitable for large-scale production and continuous or semicontinuous operation Suitable to prevent droplet breakup	High dispersed phase concentration is obtained after a long time of operation
Pulsed-flow ME 	Suitable for large-scale production and continuous or semicontinuous operation Able to prevent droplet breakup High dispersed phase concentrations obtained in a single pass	—
Rotating ME 	Suitable for large-scale production and continuous or semicontinuous operation Able to prevent droplet breakup High dispersed phase concentrations obtained in a single pass	Complicated and more expensive design Higher power consumption

(continued)

Emulsification by Membrane Operations, Table 1 (continued)

	Advantages	Disadvantages
Vibrating ME 	Suitable for large-scale production and continuous or semicontinuous operation Able to prevent droplet breakup	Complicated and more expensive design Higher power consumption Nonuniform temporal distribution of shear stress on the membrane surface
Static membrane emulsification		
	Simple experimental setup Low energy input Able to prevent droplet breakup	Emulsion production at batch scale The production of uniform droplets is possible only at low dispersed phase flux with low productivity

(*stirred membrane emulsification*) (Stillwell et al. 2007). The use of static turbulence promoters in cross-flow membrane emulsification allows increasing the shear stress at the membrane surface while maintaining a low value along the circuit out of the membrane (Koris et al. 2011). Alternatively, a periodic flow pulsation is generated in the continuous phase without recirculation (*pulsed-flow membrane emulsification*) (Holdich et al. 2013). Moving membranes can be used instead of the commonly used stationary membranes. The droplet detachment from the membrane surface is controlled by rotating (Vladislavljević and Williams 2006) or vibrating (Holdich et al. 2010) the membrane within an otherwise static continuous phase. Membrane operations used for the production emulsion droplets are described in Table 1.

Emulsification by membrane operation is controlled by:

- Membrane parameters, including porosity, mean pore size, pore geometry, pore distance, and membrane surface wettability
- Phase parameters, including interfacial tension, emulsifier type and concentration, viscosity and density of dispersed and continuous

phases, phase composition, pH, and ionic strength

- Process parameters, including wall shear stress, transmembrane pressure, membrane module configuration, and temperature

Comparing to the conventional emulsification processes, emulsification by membrane operation permits to obtain a better control of droplet size and droplet size distribution, low energy and material consumption, and modular and easy scale-up. Nevertheless, productivity (m³/day) is much lower, and therefore the challenge in the future is the development of new membranes and innovative membrane operations to keep the known advantages and maximize the productivity.

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Emulsifier

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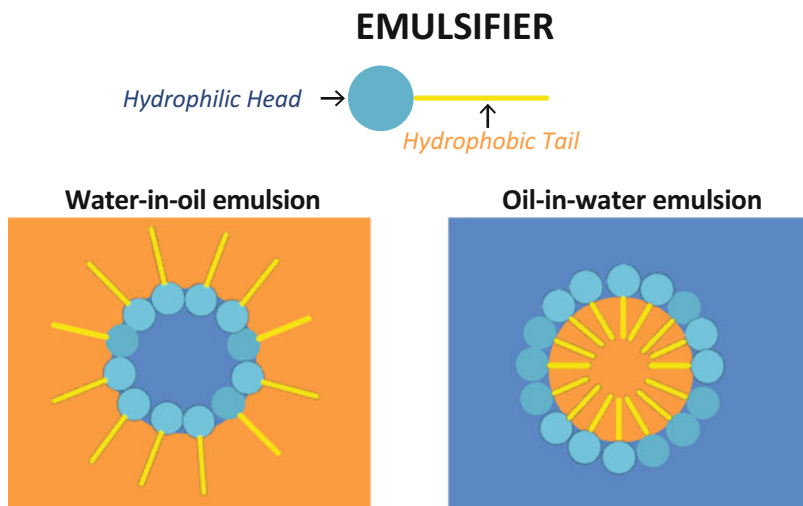
Emulsifiers are a class of molecules with surface active properties (Dickinson 2009). This behavior is due to their amphiphilic structure which

contains both a polar or hydrophilic head and a nonpolar or hydrophobic tail (Fig. 1). A measure of the degree to which an emulsifier is hydrophilic or lipophilic is given by the hydrophilic-lipophilic balance (HLB) determined by calculating values for the different regions of the molecule. Emulsifiers adsorb at interfaces between two immiscible liquid anchoring its hydrophilic part into water and its lipophilic part into oil decreasing the interfacial tension between them (Fig. 1). This facilitates droplets disruption during homogenization and, in the case of membranes, lowering the minimum emulsification pressure. Emulsifiers have an important role in emulsion stabilization against droplets coalescence and/or aggregation providing electrostatic repulsion, steric repulsion, and/or strength to the interfacial layer of the droplets.

Emulsifiers are normally classified according to the head group type as ionic (anionic and cationic), nonionic, and amphoteric (zwitterionics). Anionic emulsifiers contain anionic functional groups at their head, such as sulfate (sodium dodecyl sulfate, SDS), sulfonate, phosphate, and carboxylates. Cationic emulsifiers contain cationic functional groups at their head, such as pH-dependent primary, secondary, or tertiary amines and permanently charged quaternary ammonium cation (cetyl trimethylammonium bromide, CTAB). Nonionic emulsifiers have polar headgroups and they include glycol and glycerol esters, polyoxyethylene esters,

Emulsifier,

Fig. 1 Emulsifier structure and emulsifier distribution at water-in-oil and oil-in-water emulsion interface



polyoxyethylene ethers, polyoxyethylene–polyoxypropylene copolymers, sorbitan derivatives, and sucrose esters. Zwitterionic (amphoteric) emulsifiers have both cationic and anionic centers attached to the same molecule. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. The anionic part can be more variable and include sulfonates, sultaines, betaines, and phosphates (lecithin).

A variety of emulsifiers are natural products derived from plant or animal tissue such as hydrocolloids (high molecular weight polysaccharides) and proteins.

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Emulsifiers

► Amphiphilic Molecules

Emulsion

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An emulsion consists of two immiscible liquids (usually oil and water) with one of the liquids (dispersed phase or internal) dispersed as a form of spherical droplets in the other (continuous phase or external) (Israelachvili 1994). Depending upon the nature of the dispersed phase, the emulsions are classified as (i) oil-in-water emulsions (O/W) consisting of oil droplets dispersed in an aqueous phase and (ii) water-in-oil emulsions (W/O) consisting of aqueous droplets dispersed in an oil phase. It is also possible to prepare various types of

multiple emulsions, for example, water-in-oil-in-water emulsions (W/O/W), in which water droplets are dispersed within larger oil droplets which are themselves dispersed in an aqueous phase and oil-in-water-in-oil emulsions (O/W/O) consisting of oil droplets dispersed in larger water droplets which are themselves dispersed in an oil phase.

The preparation of an emulsion is termed emulsification and the agents used for this purpose are termed emulsifiers. Other agents, such as emulsion promoters or stabilizers, are often added to an emulsion to promote the emulsifying process, for example, by increasing the viscosity or providing a protective colloid action. The preparation of emulsions involves breaking up the internal phase by supplying mechanical or chemical energy. When an emulsion is formed, the interface between the phases is considerably increased as a result of the droplet formation. The liquid always tends to reduce its surface or interface to a minimum; therefore, an increase in interface is possible only if energy is supplied. The work that must be expended on drop division is:

$$dA = \gamma dI$$

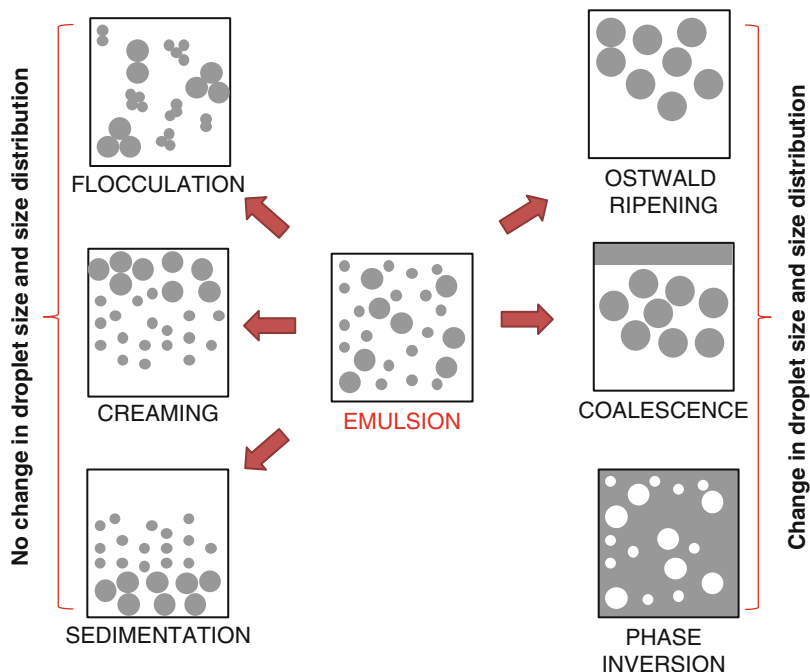
where dA is the work to be expended and dI is the increase in interface. The proportionality factor is the interfacial tension γ between the phases to be emulsified. Thus, if the interfacial tension between the two phases is high, considerable mechanical energy is required for emulsification unless an emulsifier is added; if the interfacial tension is low, little mechanical energy is consumed.

According to the droplet size, emulsions are classified as follows:

- Macroemulsions: these usually have a size range of 0.1–5 μm .
- Nanoemulsions: these usually have a size range of 20–100 nm.
- Micellar emulsions or microemulsions: these usually have a size range of 5–50 nm.

If the droplet size exhibits a wide statistical distribution, the emulsion is described as polydisperse, in contrast to monodisperse systems with a

Emulsion, Fig. 1 The various breakdown processes in emulsions



uniform droplet size. The ideal particle size depends on the available methods of preparation and industrial application in each case. Another important emulsion property is the ratio of the volume of the dispersed phase (V_i) to the volume of the continuous phase or (V_c) is called the phase volume ratio (Φ). If $\Phi < 0.43$ ($V_i = 30\%$ of total volume), the flow properties of the emulsion are determined primarily by the continuous phase. If $\Phi > 0.43$, the viscosity of the emulsion generally increases. As Φ increases, either phase reversal or cream formation occurs.

Emulsion stability should match its application. Thus, for a number of applications, the emulsion should be stable under very specific conditions, but it should break after its purpose has been achieved according to a specific condition (such as temperature, pH, or salts, or the like). An emulsion is stable if fusion of the droplets is prevented by a sufficiently high energy barrier (Tadros 2013). In general, the energy barrier is built up by the film of emulsifier that forms at the surface of the droplets. Several breakdown processes may occur on storage depending on

particle size distribution and density difference between the droplets and the medium (Fig. 1).

In sedimentation, the uniform dispersion of the droplets is disturbed by aggregation, which leads to settling or creaming of the internal phase. This process results from external forces usually gravitational or centrifugal. When such forces exceed the thermal motion of the droplets (Brownian motion), a concentration gradient builds up in the system with the larger droplets moving faster to the top (if their density is lower than that of the medium) or to the bottom (if their density is larger than that of the medium) of the container. To keep an emulsion stable, such aggregation must be prevented since droplet aggregates sediment faster than individual small droplets. Sedimentation is not always necessarily accompanied by coalescence. Although the distribution has been altered, the original dispersion can be restored by shaking or stirring. Flocculation refers to aggregation of the droplets (without any change in primary droplet size) into larger units. It is the result of the van der Waals attraction that is universal with all disperse systems. Flocculation

occurs when there is no sufficient repulsion to keep the droplets apart to distances where the van der Waals attraction is weak. Flocculation may be “strong” or “weak,” depending on the magnitude of the attractive energy involved. One way to overcome the van der Waals attraction is by electrostatic stabilization using ionic surfactants, which results in the formation of electrical double layers that introduce a repulsive energy that overcomes the attractive energy. The second and most effective method of overcoming flocculation is by “steric stabilization” using nonionic surfactants or polymers. Ostwald ripening (disproportionation) results from the finite solubility of the liquid phases. Liquids that are referred to as being immiscible often have mutual solubilities that are not negligible. With emulsions, which are usually polydisperse, the smaller droplets will have larger solubility when compared with the larger ones (due to curvature effects). With time, the smaller droplets disappear and their molecules diffuse to the bulk and become deposited on the larger droplets. With time, the droplet size distribution shifts to larger values. Several methods may be applied to reduce Ostwald ripening: (i) Addition of a second dispersed phase component that is insoluble in the continuous medium. In this case, partitioning between different droplet sizes occurs, with the component having low solubility expected to be concentrated in the smaller droplets. During Ostwald ripening in a two-component system, equilibrium is established when the difference in chemical potential between different size droplets (which results from curvature effects) is balanced by the difference in chemical potential resulting from partitioning of the two components. This effect reduces further growth of droplets. (ii) Modification of the interfacial film at emulsion interface. By using surfactants that are strongly adsorbed at the emulsion interface (i.e., polymeric surfactants) and that do not desorb during ripening (by choosing a molecule that is insoluble in the continuous phase), the rate could be significantly reduced. In coalescence, the individual droplets fuse together. First, the smaller droplets are

absorbed by the larger droplets, and then increasingly larger drops merge together until two continuous phases are finally formed. The driving force for coalescence is the surface or film fluctuations which results in close approach of the droplets whereby the van der Waals forces is strong thus preventing their separation. Two droplets can only coalesce if the intervening layer of liquid is pierced when they approach each other. Therefore, coalescence is opposed in two ways by the emulsifier film surrounding the droplets. First, as in the case of aggregation, the like charges of the electrical double layer prevent them from approaching each other. Second, the buildup of an elastic surface film causes the emulsion droplets to bounce off each other when they collide. Coalescence is always followed by accelerated settling or creaming, which destroys the emulsion completely. The emulsion is then broken and cannot be reconstituted by shaking or stirring. The driving force for prevention of coalescence is to produce a stable film that can be achieved by two mechanisms and their combination: (i) increased repulsion both electrostatic and steric and (ii) dampening of the fluctuation. In general, smaller droplets are less susceptible to surface fluctuations and hence coalescence is reduced. This explains the high stability of nanoemulsions. The phase inversion refers to the process whereby there will be an exchange between the disperse phase and the medium. For example, an O/W emulsion may with time or change of conditions invert to a W/O emulsion. In many cases, phase inversion passes through a transition state whereby multiple emulsions are produced. Phase inversion of emulsions can be one of two types: transitional inversion induced by changing the factors that affect the HLB of the system, for example, temperature and/or electrolyte concentration, and catastrophic inversion, which is induced by increasing the volume fraction of the disperse phase.

Emulsions have application in several industrial systems such as food emulsion, for example, mayonnaise, salad creams, deserts, and beverages; personal care and cosmetics, for example,

hand creams, lotions, hair sprays, and sunscreens; and pharmaceuticals, paints, and bitumen emulsions.

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Emulsion Characterization

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The production of emulsions via membrane processes is investigated since 30 years and started with investigations from Nakashima et al. with porous glass membranes (Nakashima et al. 1991). There are several principles of membrane emulsification as, e.g., direct emulsification and premix emulsification. But nevertheless which process is used, the characterization of the emulsion is an important issue.

Besides the emulsion's ingredients, which are defined by the manufacturer, there are many structure parameters which influence the physical stability, the color, the rheological behavior, or the controlled release properties of the emulsion.

If the kind of emulsion is not known, the first characterization method must identify if it is an oil in water (o/w) or water in oil (w/o) emulsion. In many cases this can be easily done by a dilution test. This means that an o/w emulsion can be diluted with a hydrophilic phase and w/o emulsions can be diluted with a hydrophobic phase. Measurement of conductivity of the emulsion is another possibility as o/w emulsions have in general a much higher conductivity than w/o emulsion.

These tests cannot identify if a double emulsion (e.g., oil in water in oil phase) is present. This must be investigated with microscopic methods.

The two main characteristics of an emulsion, which influence the physical stability, the color, and the rheological behavior, are the drop size distribution (DSD) and the disperse phase content (DPC) (Schuchmann 2007).

The DPC is set by the manufacturer and is constant when using premix membrane emulsification. Using other membrane emulsification processes like cross flow devices, the DPC of emulsions is adjusted by the rate of flow of the oil and water phase or by recirculation time of the continuous phase/emulsion and changes continuously. Regarding multiple emulsions, additional instability mechanisms may lead to changes of DPC while emulsifying and storing. The DPC can be measured with differential scanning calorimetry (DSC) (Schuch et al. 2013; Dalmazzone et al. 2009), NMR (Bernewitz et al. 2011; van Duynhoven et al. 2007), or rheological characteristics of single and double emulsions.

The DSD depends on several factors as the kind and pore size of the membrane, the transmembrane flux, the shear forces at the membrane surface, as well as the composition of the emulsion (kind of emulsifier, viscosity of the phases, etc.). The DSD can be measured with various methods which are referred here. The DSD can also change during storage and distribution of an emulsion leading to a product deterioration and phase separation. A rough indication for the physical stability of an emulsion can be the zeta potential (ζ), whereas $\zeta > 30$ mV indicates a stable emulsion. Another method is a Dynamic Mechanical Analysis (DMA) of the emulsion (Brummer 2006).

As the changes of DSD are often very slow and cannot be monitored over the whole shelf life of a product, there are several test procedures to accelerate this process. A procedure is to rise the storage temperature from room temperature to 40–50 °C which accelerates the deterioration processes by the factor 2. Other means are the exposure of the emulsion to many short temperature abuses or to a centrifugal field which can shorten the monitoring time by the factor 10–2,000. It should be kept in mind that all the acceleration

techniques may change the structure of the emulsion and may lead to differing results compared to real storage conditions.

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Emulsion Liquid Membrane (ELM)

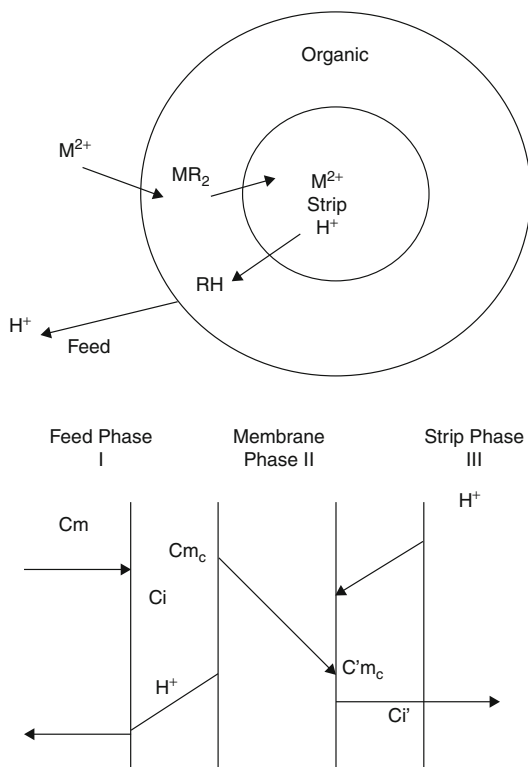
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Emulsion liquid membrane, ELM, is a system in the form of double emulsions (for details, see Chakraborty et al. 2010). It may be of two types: water-in-oil emulsion dispersed in an external

aqueous phase and oil-in-water emulsion dispersed in an outer organic phase. The membrane phase in the water-in-oil-in-water (W/O/W) type is the immiscible oil phase separating the aqueous phases, while in the O/W/O type, the immiscible water phase separating the two organic phases acts as the LM. Hence, the liquid membrane serves here a dual purpose: (a) permitting selective transfer of one or more components through it from external phase to internal droplets and vice versa and (b) preventing mixing of external and internal phases. The emulsion is dispersed in the feed solution, and mass transfer from the feed to the internal receiving phase takes place. ELMs were first used for separation of hydrocarbons from wastewater with high separation efficiency. Compared to conventional processes, emulsion liquid membrane (ELM) process has some attractive features, for example, simple operation, high efficiency, extraction and stripping in one stage, larger interfacial area, and scope of continuous operation.

Since an ELM is a thin film of liquid (oil or aqueous) composed of surfactants and their solvents between a feed and a receiving phase, any immiscible liquid can serve as a membrane between two liquid or gas phases containing a solute at different concentrations. If the solute is soluble in the membrane phase and has a reasonable diffusivity through the membrane, then its selective transport through the membrane from higher to lower concentration can be achieved. This type of permeation has simple mechanism and not of much technical importance.

At facilitated transport mechanism, liquid membrane incorporates a reactive component or carrier, reacting reversibly and selectively with species of interest to carry the formed complexes across the LM to the internal phase, and dissociates, discharging the solute to the internal phase. The unchanged carrier then diffuses back to the membrane-external phase interface (see Fig. 1). A small amount of carrier is required in the membrane phase even for achieving a high degree of separation. At different proton concentrations in the aqueous phase or using another ions, ion exchange processes between two LM surfaces occur. This phenomenon is called coupled mass transport. If the transports of these two different species occur



Emulsion Liquid Membrane (ELM), Fig. 1 Schematic representation of the liquid membrane globule and concentration profile of solute through ELM

in the same direction, it is called cotransport, while transport in opposite direction is called countertransport. Evidently the process leads to the transport of targeted ionic species across the membrane against their concentration gradient. This so-called “uphill” transport will continue until one driving factor (difference of chemical potentials) is balanced by the difference between chemical potentials of another transported ion.

The ELM technique has great potential for recovery and removal of different metal ions. Separation of metals like copper, zinc, cadmium, cobalt, nickel, mercury, uranium, chromium, rhenium, and several others, including noble metals like gold and silver, lanthanides, and rare earths, was studied. To date, there are two industrial plants installed for zinc recovery from wastewater in Austria, having a capacity of 75 m³/h and 700 m³/h, removing zinc selectively from 500 to 3 ppm. Bis(2-ethylhexyl) dithiophosphoric acid

has been used as carrier. One more plant with the 200 m³/h capacity in Germany and the 200 m³/h capacity plant in the Netherlands.

Weak acids like phenol and cresol and weak bases like ammonium and amines have been successfully removed from wastewater. Among them, the separation-concentration of phenol has been intensively investigated. Phenol removal from wastewater was commercialized in China. Phenol is removed from about 1,000 ppm to 0.5 ppm with an extraction efficiency of greater than 99.95 %.

ELM technology has been applied to a great extent for separation of mixtures of saturated and aromatic hydrocarbons, of amino acids, and of strong acids like nitric acid and thiocyanate. Cyanide removal from wastewater in gold processing is commercialized in China. Cyanide is reduced from about 130 ppm to 0.5 ppm with an extraction efficiency of 99.6 %.

ELM has promise in the fields of biotechnology and biomedicine and has found application in the separation of organic acids, fatty acids, purification of antibiotics, enzyme-catalyzed reactions, and detoxification of blood.

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Emulsion Liquid Membrane for Wastewater Treatment

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Emulsion liquid membranes are known as double emulsion system. The advantage of this process is extraction and stripping process occurred

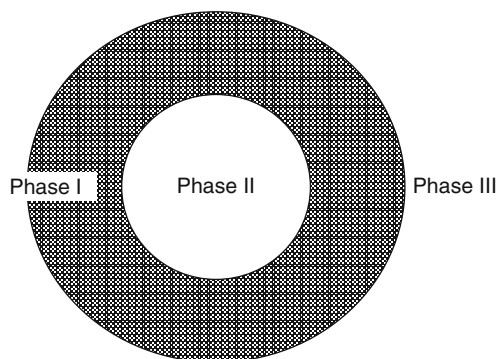
simultaneously in one single-step operation, and equilibrium limitation can be removed. It also can reduce the amount of expensive extractant; high fluxes and high selectivity are possible. It is also possible to treat any source of wastewater containing organics and metals even at low concentration. The primary emulsions of water in oil emulsion were prepared by emulsifying two immiscible phases of the stripping solution and organic liquid membrane phase with a surfactant to produce an emulsion. This primary emulsion is then dispersed in the solution or phase to be treated. Mass transfer takes place between the feed phase and the internal phase through the liquid membrane phase. The illustration and schematic diagram of the process is shown in Fig. 1. The organic liquid membrane may contain a carrier to facilitate the extraction process. The carrier will act as a shuttle to carry the solute from external interface to the internal interface or receiving

phase. At the external interface, the carrier will form carrier-solute complexes and diffuse to the internal interface and release the solute into the receiving phase by the reaction with the stripping agent. For example, in metal separation from wastewater, even in very low concentration, the carrier will selectively combine with the solutes to form a metal-carrier complex, and the complex will permeate through the membranes from the outer to the inner interface. At the inner interface, the complex decomposes by the reversal of the equilibrium reaction, and the metal ion is liberated into the internal phase and the regenerated carrier goes back into the membrane phase. The mechanism of removal and recovery of the solute/metal assisted by the carrier is illustrated in Fig. 2.

The major problem associated with ELMs in the wastewater treatment is emulsion stability. If the emulsion globules break and the inner droplet phase spills into the continuous phase, the separation is lost. Interfacial shear between the continuous phase and membrane phase causes the liquid membrane to thin and, in some cases, rupture.

Another problem is osmotic swelling although it is rarely mentioned in the literature. This phenomenon occurs when water in external phases diffuses through the organic membrane phase and swells the inner aqueous droplet phase. The increased volume of the internal phase leads to increased breakage and dilution of the concentrated solute in the droplet phase.

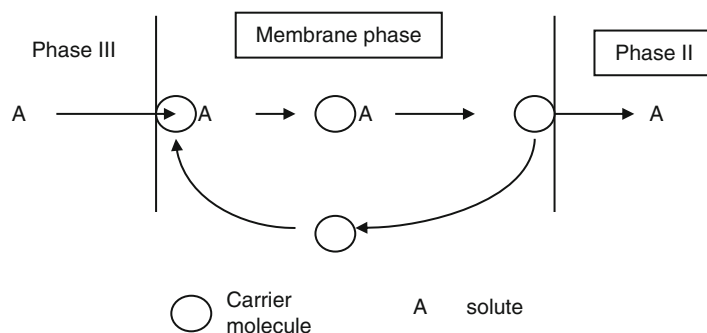
For the last three decades, this method has attracted many studies in the area of hydrometallurgy such as separation of metal ions either from wastewater or from ores (Othman et al. 2006; Reis and Carvalho 1993; Reed et al. 1987; Marr 1984;



Emulsion Liquid Membrane for Wastewater Treatment, Fig. 1 A schematic diagram of emulsion liquid membranes

Emulsion Liquid Membrane for Wastewater Treatment, Fig. 2

The mechanism of couple transport in emulsion liquid membrane



Draxler and Marr 1986; Babcock et al. 1986). It has been reported that emulsion liquid membrane system has been successfully used to recover copper selectively from waste stream of mine solutions (Wright et al. 1995).

From the viewpoint of practical application in wastewater treating processes, recovery processes for copper (Volkel et al. 1980; Goto et al. 1989a), uranium (Hayworth et al. 1983), and zinc (Marr 1984) were examined in test plant. The first application of emulsion liquid membrane (ELM) on an industrial scale was the process to remove zinc from wastewater at a textile plant in Austria (Draxler and Marr 1986).

In order to get a better understanding of emulsion liquid membrane process and the system potentials, the extraction performance must be studied based on the kinetics and thermodynamic aspects. The parameters that affect the solute extractability and selectivity should be identified. The parameters such as stripping agent types and acidity that control the mass transfer of solute, volume ratio of emulsion to external phase that affects the mass transfer area of extraction process, and carrier concentration, type of diluents, swelling, residence time, and agitation rate that control the extraction performance and the breakup rate of emulsion should be studied.

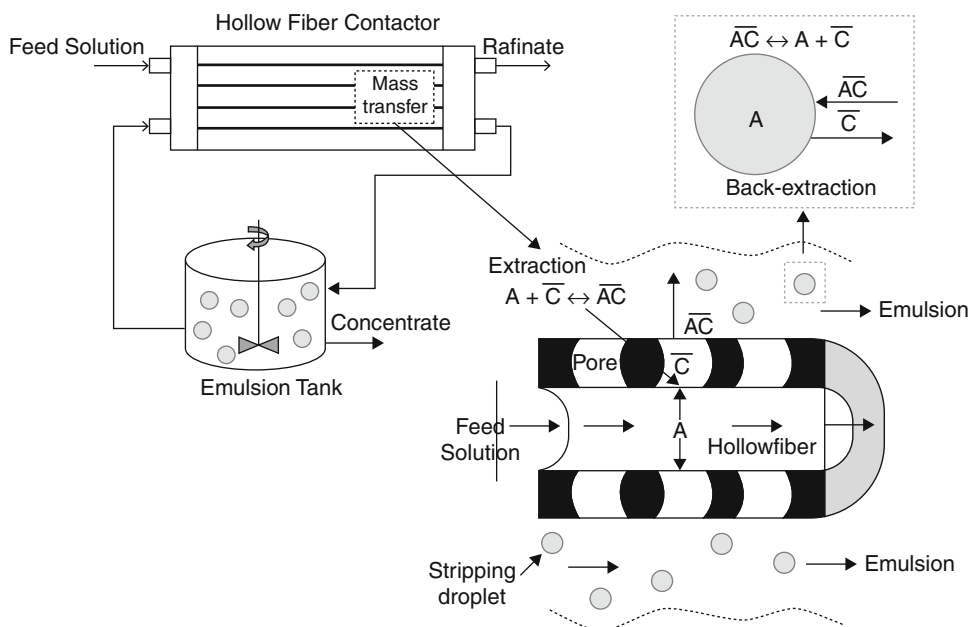
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Emulsion Pertraction Technology for Zinc Recovery

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The emulsion pertraction technology (EPT) is a separation process that combines the ability of liquid membranes to promote the uphill transport of target species by the coupling between mass transfer and chemical reaction and the benefits of using membrane contactors, namely, large interfacial area, nondispersive contact, and independent flow of the fluid phases. Figure 1 shows the flow diagram of the EPT process that comprises two essential process units: a microporous hollow fiber membrane contactor (see Fig. 2) and the emulsion vessel that contains a pseudo-emulsion consisting of the organic phase formulated with a selective organic carrier and the dispersed stripping solution. The target solute is chemically transferred from the aqueous feed to the organic phase that is embedded in the pores of the hollow fibers due to their hydrophobic character. Next, the solute-carrier complex diffuses to the interface between the organic and the droplet of stripping phase where the back-extraction reaction occurs. The solute is recovered from the internal aqueous phase after emulsion settling (San Román et al. 2010; Urtiaga et al. 2010; Carrera



Emulsion Pertraction Technology for Zinc Recovery, Fig. 1 Performance of the EPT process

et al. 2009; Bringas et al. 2006; Uriaga et al. 2005; Klaassen and Jansen 2001). In the forthcoming section, the potential of the EPT technology to develop separation processes with zinc recovery is evaluated.

Recovery of Zinc from Liquid Wastes by EPT

Zinc's electropositive nature makes it well-suited for use as a coating for protecting iron and steel products from corrosion. For this reason, the surface treatment industry accounts for almost half zinc modern-day demand. The processes involved in the surface treatment of components are predominantly water-based, and thus the generation and management of complex liquid wastes is an issue of concern (Bringas et al. 2012). EPT has been proven to be an efficient technology to perform both the selective removal and recovery of zinc from different wastes produced in the context of surface treatment industry: (i) spent pickling acids (SPA) generated in the hot-dip galvanizing process (see composition in Table 1) and (ii) spent chromium-based passivation baths (SPB)

employed in zinc electroplating operations (see composition in Table 1).

Figures 3 and 4 depict the separation and recovery objectives to be achieved by the application of EPT to the treatment of SPA and SPB.

Under the usual composition of SPA, zinc forms anionic chlorocomplexes ($ZnCl_4^{2-}$ and $ZnCl_3^-$) while iron is present in the form of neutral or cationic compounds (Regel et al. 2001). Tributyl phosphate (TBP) and water are reported as the most suitable extraction and back extraction reagents enabling the selective separation and concentration of zinc with minimum iron extraction (Cierpezewski et al. 2002). On the other hand, the information provided by the equilibrium isotherms depicted in Fig. 5 confirms the commercial selective carrier bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) as a suitable reagent to formulate the liquid membrane due to its capacity to selectively separate Fe^{3+} and Zn^{2+} (tramp ions) from chromium under the typical pH conditions (1.8–2.5) of the passivation baths. Sulphuric acid is selected as stripping agent (Uriaga et al. 2010).

Figure 6 shows the kinetic results obtained with the SPA-TBP-water and the EPT process.

Emulsion Pertraction Technology for Zinc Recovery,

Fig. 2 Characteristics of hollow fiber contactors for a bench scale EPT process



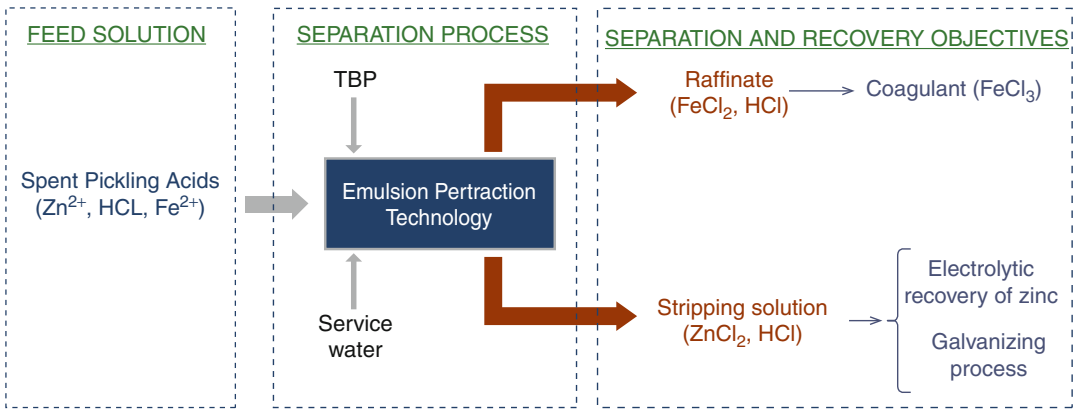
Parameter/Characteristic	Value/Description
Fiber material	Polypropylene
Shell material	Polypropylene
Type of fiber	X-50
Internal diameter of the fiber	240 μm
Thickness	30 μm
Average pore diameter	0.04 μm
Porosity	40%
Effective lenght	0.15
Interfacial area	1.4 m^2
Number of fibers	10200

Emulsion Pertraction Technology for Zinc Recovery,

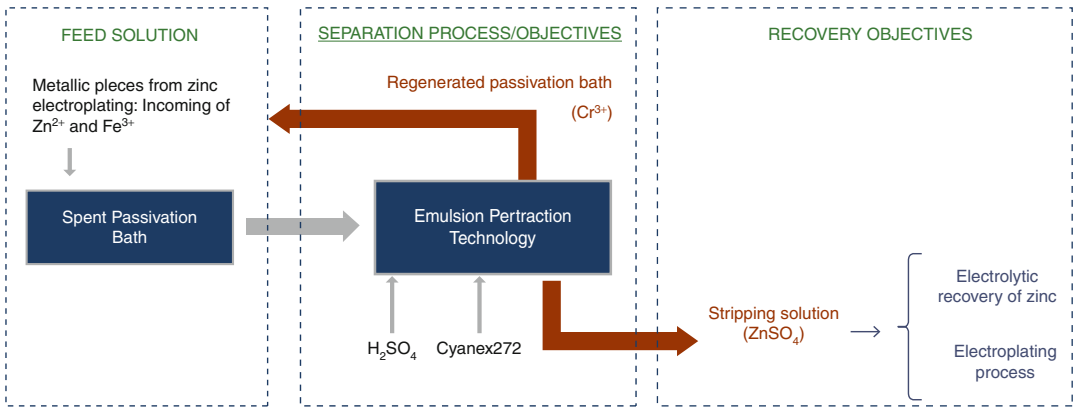
Table 1 Physical-chemical properties of spent pickling acids (SPA) and spent chromium-based passivation baths (SPB)

SPA		SPB	
Parameter	Value	Parameter	Value
pH	≈ 0	pH	1.8–2.5
Zn^{2+} (mg/L)	122,000	Zn^{2+} (mg/L)	2500–11,780
Fe^{2+} (mg/L)	100,000	Fe^{3+} (mg/L)	20–90
Cl^- (mg/l)	300,000	Cr^{3+} (mg/L)	4500–9350
Free acidity, H^+ (mol/L)	1	NO_3^- (mg/L)	67,520

It is concluded that the extraction (EX) and back-extraction (BEX) percentages of zinc and iron, when steady state conditions (regarding zinc kinetics) are reached, are respectively, 79 % (EX Zn), 98 % (BEX Zn), 23 % (EX Fe), and 38 % (BEX Fe). Under these operation conditions, the maximum value of selectivity of zinc over iron in the stripping solution is 15 kg of Zn/kg of iron (Ortiz et al. 2004; Samaniego et al. 2006; Samaniego et al. 2007; Carrera et al. 2009; Bringas et al. 2012). On the other hand, the efficiency of the EPT process to carry out the regeneration of real passivation baths is demonstrated in Fig. 7 which shows reductions



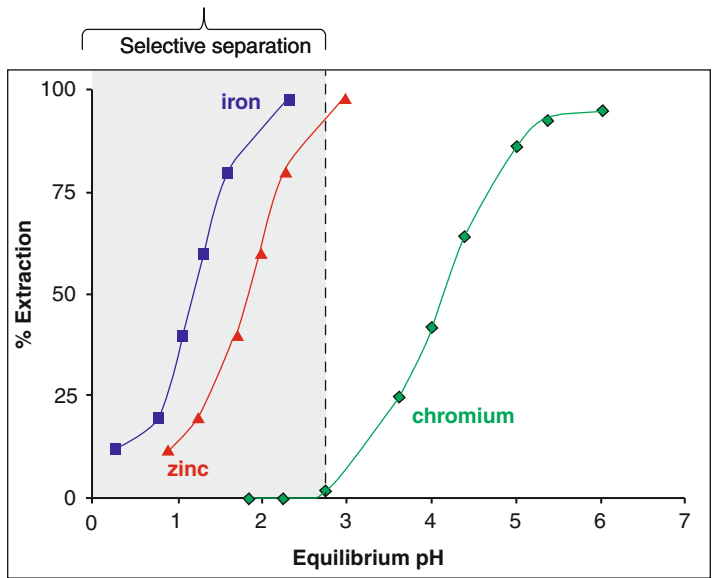
Emulsion Pertraction Technology for Zinc Recovery, Fig. 3 Treatment of spent pickling acids by EPT with zinc recovery



Emulsion Pertraction Technology for Zinc Recovery, Fig. 4 Regeneration of chromium-based passivation baths by EPT with zinc recovery

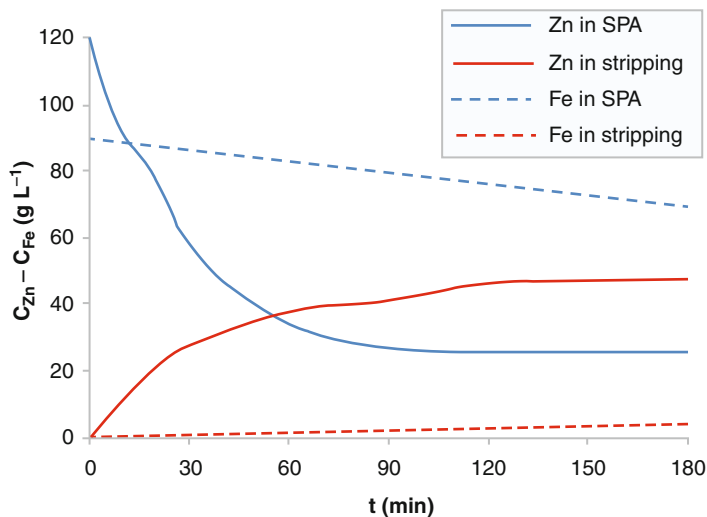
Emulsion Pertraction Technology for Zinc Recovery,

Fig. 5 Extraction isotherms of iron, zinc and chromium with Cyanex272



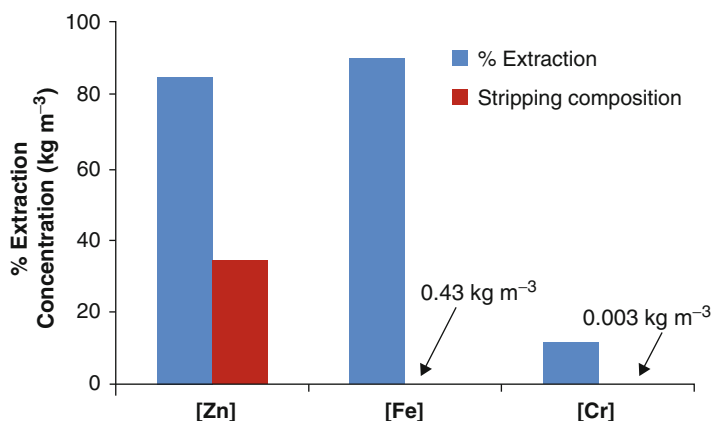
Emulsion Pertraction Technology for Zinc Recovery,

Fig. 6 Evolution with time of iron (discontinuous line) and zinc (continuous line) concentration in the SPA and stripping solution (0.5 L of SPA with the composition indicated in Table 1; 1 L of organic solution containing 50 % v/v TBP in Shellsol D70; 1 L of water)



Emulsion Pertraction Technology for Zinc Recovery,

Fig. 7 Extraction percentages and concentrations in the stripping solution after 3 h of EPT regeneration of SPB using Cyanex272 as selective extractant



in the zinc and iron contents higher than 80 % after 3 h of experimental running with an almost negligible variation of the chromium concentration. Furthermore, zinc is selectively recovered in the stripping solution (concentration $>35 \text{ kg/m}^3$) being the concentrations of iron ($<0.45 \text{ kg/m}^3$) and chromium ($<0.003 \text{ kg/m}^3$) almost negligible (Urriaga et al. 2010; Bringas et al. 2011; Diban et al. 2011; Bringas et al. 2012).

Therefore, these results confirm the EPT process as a suitable alternative to perform the treatment of spent pickling acids and spent passivation baths allowing at the same time the zinc recovery for further reuse as was illustrated by Figs. 3 and 4.

Future Directions

Future development will require research and development activities in the following areas:

1. Determination of the optimal operational conditions to: (i) maximize the extraction and back-extraction kinetics and (ii) achieve maximum values of selectivity which permit the exploitation of the different process streams generated after the application of the EPT process.
2. Analysis of the long-term performance of the separation process to evaluate the stability of the selective carrier which guarantees the process' economic viability.

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Emulsion Rupture by Membranes

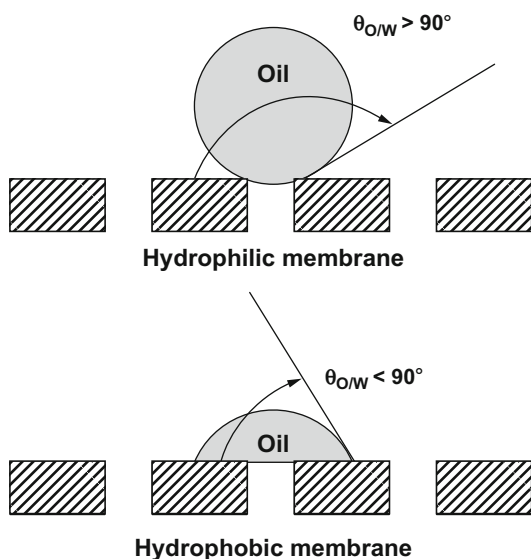
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Emulsions are homogeneous mixtures that consist of a dispersed phase (oil droplets in O/W emulsions) distributed uniformly in a continuous phase (water). Ultrafiltration (UF) and microfiltration (MF) membranes have been used for the treatment of O/W emulsions produced in industries such as steel works, metal finishing, pharmaceuticals, cosmetics, food, etc. Oil droplets are recovered as retentate and the aqueous phase permeates the membrane. The production of 1 t of steel may demand up to 200 t of water, the largest water usage corresponding to the rolling mills. Membrane performance diminishes when oil droplets fall below the micron range and problems become more pronounced when ionic surfactants are present, as they increase repulsive forces between droplets.

Demulsification is commonly achieved by chemical or electrostatic methods. Chemical demulsification destabilizes the disperse phase by two mechanisms: *coagulation* (inorganic salts) and *flocculation* (organic polymers). The disadvantage of chemical demulsification is that the bulk phase has to be further treated before discharge. Electrostatic demulsification is ineffective for emulsions with high water content and sparking during treatment may generate new compounds from the surfactant and the oil. However, membranes can be used as coalescers by forcing the emulsion through the pores of the membrane (Kajitvichyanukul et al. 2011).

Hydrophilic membranes induce coalescence of O/W emulsions while hydrophobic membranes can be used for the demulsification of W/O emulsions (Fig. 1). The main factors affecting membrane demulsification are (Daiminger et al. 1995; Hong et al. 2003; Kocherginsky et al. 2003):



Emulsion Rupture by Membranes, Fig. 1 Influence of membrane characteristics in oil droplet rejection

- Membrane pore size, transmembrane pressure (ΔP), and imposed in-pore shear rates affect coalescence. The smaller the membrane pore size and the lower ΔP , the better demulsification efficiency. However, small pores coupled with a low ΔP would lead to low permeation flux.
- If the ΔP is below a critical value (ΔP_c), the emulsion rejection can be maximized. Above a ΔP_c the membrane acts as a coalescer and the droplets wet the membrane enabling the oil droplets to coalesce.
- Membrane demulsification seems to be independent of the initial disperse phase concentration and membrane thickness.
- The demulsification process is determined by interactions between droplets and membrane surface.

So far, membranes as coalescers do not show great advantages with respect to conventional coalescing techniques, e.g., fiber-bed coalescence and electrostatic coalescers. New chemically treated ceramic membranes and silicon carbide supports have a great potential for oil-water applications since they are abrasion and solvent

resistant, easy to clean by backflushing, and have a low cost and longer life than the previous generation membranes.

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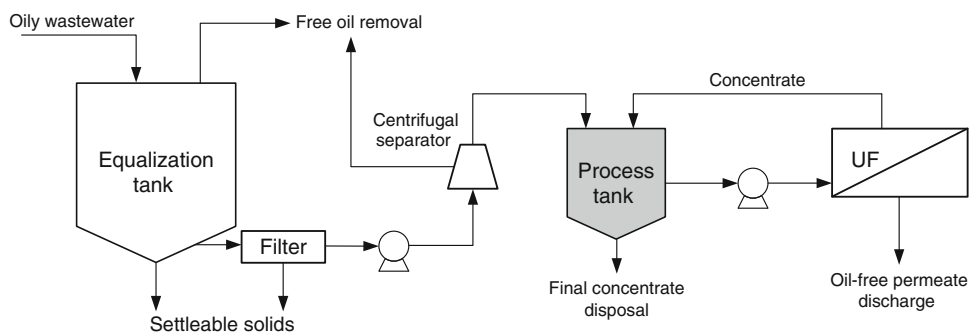
Emulsion Separation by Membranes

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Separation of oily emulsions from wastewaters is generally carried out by a combination of chemical and mechanical methods. Chemicals (coagulants and flocculants) are used to destabilize the oil-water interface allowing the oil droplets to coalesce. Mechanical methods include gravity-based settlers, skimmers, dissolved air flotation (DAF), centrifuges, electro-coalescers, etc.

Pressure-driven membrane processes (microfiltration MF, ultrafiltration UF, and reverse osmosis RO) may be used to separate oil and water phases. The water molecules move through the membrane (permeate) and a concentrated emulsion (retentate or concentrate) is obtained. Some components of the emulsion may also move through the membrane, depending on their characteristics and size and the nature of the



Emulsion Separation by Membranes, Fig. 1 Hybrid UF system for oily wastewater treatment

membrane, leading to contamination of the permeate. Fouling and scaling of the membrane lead to a poor performance and membrane cleaning procedures must be taken into account.

When MF is used for oil-water separation, particulates, emulsified oil, and microbial contaminants can be removed. Cross-flow velocities may range between 3 and 6 m/s and transmembrane pressures (TMPs) between 100 and 770 kPa. The main limitation of membrane processes is the decline of the permeate flux over time because of concentration polarization, membrane fouling (due to surfactant or oil adsorption on the pore walls), gel layer formation, pore blocking by oil droplets, pH, and temperature.

Often it is not possible to use a simple membrane system to perform an oil-water separation: some effluents may cause severe membrane fouling and pretreatment is necessary to maintain a high and steady flux. In these situations, *integrated-membrane or membrane-based hybrid processes* may be suitable alternatives to obtain good process performance and to extend membrane life (Coca et al. 2013). A typical membrane hybrid process for oily wastewaters is shown in Fig. 1.

Usually the process starts with the removal of settleable solids and free-floating oil prior to membrane treatment, mainly UF. This can be accomplished in a tank with free-oil removal equipment, such as a skimmer, or by a rotating brush strainer, a pressure or vacuum filter to remove solids, and a centrifugal separator or a hydrocyclone to remove oil and solids. The remaining oily wastewater (mainly stable O/W

emulsion) is then transferred to a process tank and pumped through the UF unit to remove the emulsified oil. The retentate containing the oil is recycled to the process tank, and the permeate is continuously withdrawn. This process is commonly used in the automobile industry (Cheryan and Rajagopalan 1998).

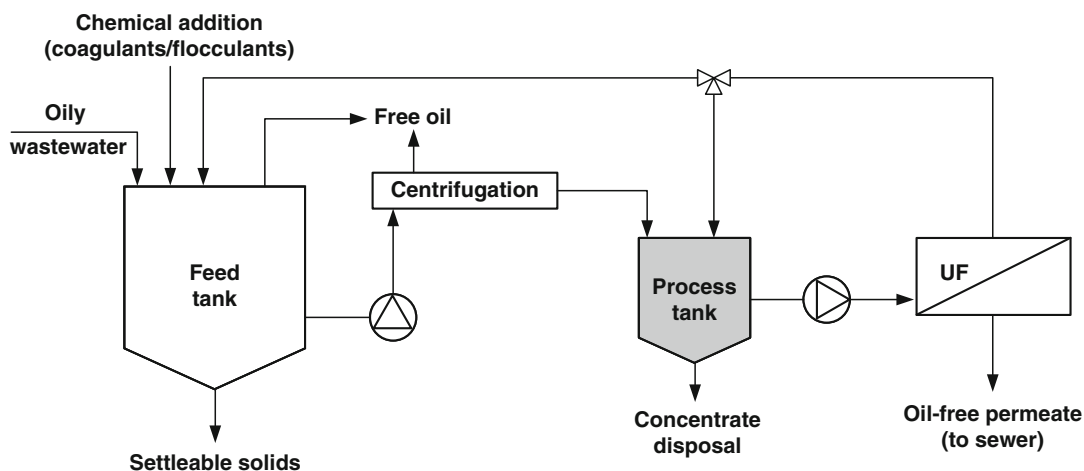
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Emulsion Treatment with Membranes

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An emulsion is a homogeneous mixture of two immiscible liquids, with one of them (typically oil) dispersed as droplets into the other. Emulsion droplets usually range between 0.1 and 20 μm in diameter. The two main categories of emulsions are



Emulsion Treatment with Membranes, Fig. 1 UF process for oily wastewater treatment

oil-in-water (O/W, >30 % water) and water-in-oil (W/O, <25 % water): water and highly polar liquids are hydrophilic, while nonpolar liquids are considered “oils”. Emulsions consist of two phases: an internal or discontinuous phase (finally divided droplets) and an external or continuous phase (which keeps the droplets in suspension), which are bound together at the interphase. A surfactant reduces the interfacial tension between the two phases binding them together. Industrial oily wastewaters can be classified as: *free oil* ($D_p \geq 150 \mu\text{m}$), *dispersed oil* ($D_p = 20\text{--}150 \mu\text{m}$), *stable emulsified oil* ($D_p \leq 20 \mu\text{m}$), and *dissolved oil* ($D_p \leq 5 \mu\text{m}$). Free oils and dispersed O/W emulsions can be removed by mechanical methods such as gravity settling, skimming, coalescence, centrifugation, etc. (Alther 1998; Stewart and Arnold 2008). Stable emulsified oils and dissolved oils cannot be removed efficiently by conventional methods because of the small droplet size and low oil concentration.

Membrane processes are increasingly being applied for treating O/W emulsions due to their advantages: high-quality permeate and removal efficiency, lower capital costs than with thermal processes, and compact design. Some of the most promising membrane O/W treatments are dehydration of emulsions by pervaporation, reverse

osmosis (RO), flocculation followed by microfiltration (MF), MF, membrane distillation, nanofiltration (NF), and ultrafiltration (UF) (Cheryan 1998; Chakrabarty et al. 2010).

A typical UF-based system for oily wastewaters, operated in a semi-batch recycle mode, is shown in Fig. 1. The final concentrate volume may be only 3–5 % of the initial oily wastewater volume. The system must be cleaned after a certain time to restore the permeate flux. O/W emulsions may be reduced by 85–90 % by volume and with an oil concentration in the retentate of 70–75 %.

MF or UF processes cannot remove dissolved oil components in water. For that purpose, other methods, such as RO or NF, are required. The choice of membrane material is important: inorganic membranes are chemically robust and expensive; polymeric membranes have lower resistance to aggressive feeds and are more susceptible to fouling, but are considerably cheaper. In spite of the fact that effluent oil concentrations of 5 ppm or less can be achieved with membranes, they have not found wide practical applications so far. Membrane systems suffer from concentration polarization and fouling problems that lead to a substantial flux decline with time. Membranes must be replaced every 3–5 years.

O/W emulsions can sometimes be treated by a combination of two membrane processes (e.g., UF/NF, UF/RO or NF/RO) to obtain a high-quality water effluent.

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Emulsions' Drop Size Distribution, Measurement of

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The drop size distribution (DSD) of an emulsion has influence on the physical stability, the color, and the rheological behavior of the emulsion and is therefore an important means of characterization.

The DSD can be measured with various methods. In principle one can distinguish between methods which measure physical characteristics of single drops or physical characteristics of the bulk emulsion. The latter are often used for the characterization of an emulsion in terms of quality control where it is only necessary to notice differences between a reference and a product or where it is sufficient to attain the DSD results only after a calibration against a system with known DSD. Examples are rheological behavior, dielectric spectrometry, dynamic scanning calorimetry, focused beam reflectance, or dynamic reflection measurements. An advantage of these methods is

often that they are fast and may be used online or at least without diluting the sample.

For the measurement of DSD, a physical characteristic which is connected to the drop size of a single drop-like sedimentation velocity, diffraction of light at the drop surface, projected area in a microscopic image, etc., is necessary. This makes clear that the basis of the calculation of DSD varies between different methods, and one should not expect the same DSD results from different measuring methods. In addition during the calculation procedure, it is partly necessary to make assumptions and simplifications, and therefore DSD results are very sensitive to the calculation parameters which are set by the manufacturer or which can be set by the user of the equipment.

The most common techniques for DSD measurement are presented in Table 1 which shows the measuring principle as well as the analyzable drop size range and some restrictions of the method.

Progress in the field of emulsions has evolved complex structures, like multiple emulsions (Muscholik 2007; Jiménez-Colmenero 2013). As in a multiple emulsion, there are more than one DSD to determine the complex structure that challenges the common measuring techniques. However, progress in the field of DSD determination of double emulsions has been made. Especially PFG-NMR and IA of confocal laser scanning microscopy images offer possibilities for the characterization of double emulsions (Schuster et al. 2012).

Another important issue in the context of DSD measurements is the illustration and interpretation. DSDs are statistical distributions and can be shown as cumulative or density distributions. Especially showing the latter, it is very important to consider all the rules of their calculation. To the authors' knowledge, there are many measurement devices with very weak software concerning this point. For simplification and interpretation of results, it is very common to show only mean values of the DSD as, e.g., the Sauter Mean Diameter or statistical values like the median or modal value. Some insights on this topic are given in (Hess 2004; Sommer 2001).

Emulsions' Drop Size Distribution, Measurement of, Table 1 Overview on the most important measurement techniques for drop size analytics in emulsions

Method	Physical characteristic for size measurement	Size range	Additional information
Sedimentation	Sedimentation velocity of a single drop	(50 nm) 1 μm –1 mm	Range for the use of centrifuges in brackets. For small drops, very high dilution necessary
(Statistical) image analytics (IA)	Projected area	(0,1 nm) 1 μm –20 mm	Size range depending on the image source. Electron microscopy in brackets. Information on structure and double emulsion detection possible. High number of drops necessary for reliable statistical analysis
Laser diffraction (LD)	Diffraction of light at the drop surface	(50 nm) 1 μm –2 mm	In brackets: with additional light sources and scattering information, necessity of complex refraction index. High dilution necessary
Dynamic laser light scattering (DLS)	Diffusion rate	1 nm–1 μm	Dispersed phase content up to 10 % possible. Drop sedimentation leads to measurement error
Pulsed field gradient nuclear magnetic resonance (PFG-NMR)	Coefficient of diffusion	0,2–100 μm	Measurement without dilution possible. Characterization of some parameters of double emulsions

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process of a particular enantiomer from a racemic mixture. The most popular reaction using the technique is esterification, where *Candida rugosa* lipase or *Candida antarctica* lipase is the biocatalyst for the reaction (Giorno et al. 2007; Lau et al. 2010). The application of membranes, especially in the production of drugs and other fine chemicals, has become a trend in recent years and it will be one of the best techniques for the bulk synthesis of such compounds (Lau et al. 2010; Li et al. 2003). Hollow fiber membrane with a particular molecular weight cutoff is the best choice to use as the immobilization matrix.

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Enantioselective Membrane

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Enantioselective membrane is a type of membrane immobilized with a particular catalyst (mainly enzyme) onto the shell side for the purpose of carrying out an in situ reaction-separation

Enantiomer Discrimination (Enantioselectivity)

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Enantiomer discrimination (or chiral discrimination) is a method used to distinguish between two enantiomers for the purpose of separating the compounds. The term is also related to enantioselectivity where it refers to the discrimination of a given reactant A when it reacts with two alternative reactants B and C or in two different ways (probably at two different sites) with a reactant B (McNaught and Wilkinson 1997). A number of methods have been established to undergo enantiomer discrimination; these include mass spectroscopy (Czerwenka and Lindner 2004; Czerwenka et al. 2004), nuclear magnetic resonance (NMR) (Gafni et al. 1998; Molabaasi and Talebpour 2011), and crystal recognition (Ballesteros et al. 1995; Huai et al. 2006; Klaholz et al. 2000). These methods have been specifically developed based on a particular compound with its own characteristics of crystal structure.

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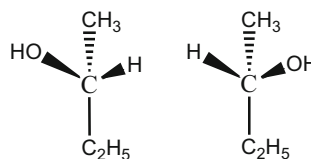
Enantiomers

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Enantiomers are types of stereoisomer whose structures are mirror image of each other, and they are not superimposable. The property is special to most chiral compounds and exists both naturally or from a particular chemical synthesis (Solomons and Fryhle 2004). It represents the intrinsic property of the building block of life, which consists of amino acids, sugars, peptides, proteins, and polysaccharides (Maier et al. 2001). The simplest compound that exhibits enantiomeric property is 2-butanol with the structural formulae given in Fig. 1.

The existence of enantiomers of a particular compound can be determined when there is a molecule containing one tetrahedral atom with four different groups attached to it, as shown in the two structures of 2-butanol above (McMurry



Enantiomers, Fig. 1 Structural formula of 2-butanol showing two different enantiomers

2004). Specialized drugs are mainly made of compounds that exhibit enantiomeric properties; these include (*S*)-ibuprofen, (*S*)-naproxen, (*S*)-citalopram, and (+)-norcisapride. As can be apparently seen, only one type of enantiomer acts as an active compound compared to their corresponding structures. This shows that the syntheses of such drugs are somewhat important, in particular, for use in pharmaceutical and medical sectors. Some of the processes carried out to obtain the compounds are tedious and require a number of reagents as well as different catalysts. This will then lead to high cost of production (Maier et al. 2001; Tramper 1996).

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Enantiomers Production by Membrane Operations

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Enantiomer production is a process of forming enantiomer of interest through membrane separation. The current method of kinetic resolution and in situ membrane separation is a highly effective process which requires less energy and short reaction time (Lau et al. 2011). Most of the works related to product separations involved lipase enzyme immobilized onto the membrane matrices. These include the production of naproxen ester (Giorno et al. 2003, 2007) and ibuprofen ester (Lau et al. 2010).

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Enantiomers Separation by Membrane Operations

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Enantiomers separation is a process of separating isomers in a racemic mixture into their individual enantiomer. The use of membranes in chiral separation can be divided into two main categories, namely, adsorption-type enantioselective membranes and membrane-assisted resolution with non-enantioselective solid membranes (Pirkle and Bowen 1994; Xie et al. 2008). The former is entirely based on the transport mechanism with an aid of chiral carriers. The work of Gumi and co-workers reported a detail account of the transfer of the (*S*)-propranolol attached to the N-hexadecyl-L-hydroxyproline through the formation of ionic pair, which is then being transported through the polysulfone-based membrane (Gumi et al. 2005). The latter is a technique mostly coupled with enzymes as biocatalysts. The enzyme is initially immobilized onto the shell side of the membrane matrix before carrying out the required resolution,

either kinetic resolution or dynamic kinetic resolution. For example, the work of Long and co-workers successfully utilized *Candida rugosa* lipase as the source of biocatalyst for the kinetic resolution of (*S*)-ibuprofen ester (Long et al. 2005).

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Enantioselective Membrane

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Enantioselective membrane is a type of membrane used to separate chiral compounds into their individual enantiomer. The usual type of membrane used for separation purposes is of polymeric type (Ceynowa 1998; Higuchi et al. 2010; Xie et al. 2008). The mechanism of chiral separation can be categorized into two different types of membranes, namely, diffusion-selective membranes and sorption-selective membranes. Diffusion-selective type of membranes are basically made of polymer without any specific chiral selectors (i.e., the polymer itself has chiral properties); however, sorption-selective membranes can be designed in such a way that a particular chiral selector can be immobilized onto the surfaces of the polymer membranes, which later gives less selective

diffusion, but provides highly selective sorption (Hadik et al. 2002; Higuchi et al. 2010).

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Enantioselective Separations, Membrane Operations

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Enantioselective separations refer to separation methods used to separate racemic mixture into individual enantiomer with the aid of membrane matrix/module. In order to measure the level of selectivity, the percent enantiomeric excess (% ee) of a mixture needs to be determined (see enantioselectivity). Membranes have been successfully used in chiral separation with various types as well as with different abilities: direct separation type of membrane made from polymer/liquid and separation with nonselective membrane assisted by chiral carriers/support (Maier et al. 2001; Pirkle and Bowen 1994).

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Enantioselective Synthesis

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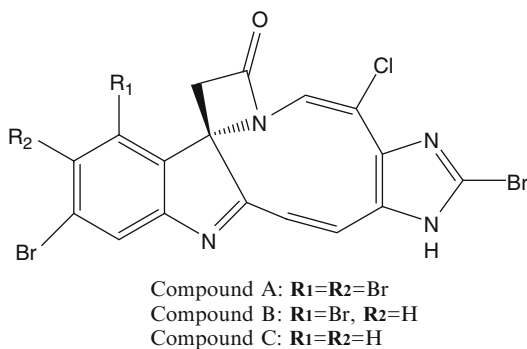
Enantioselective synthesis is a chemical/biochemical reaction where only one enantiomer of a chiral product is preferentially formed. The synthesis can be divided into two different types, namely, catalytic synthesis and biocatalytic transformation. Nowadays, chemical catalysis has been continuously improved, especially in terms of yields and percentage enantiomeric excesses (%e.e), for instance, the synthesis of spirocyclic oxindolo- β -lactam, a combination of indole and β -lactam, which acts as antibacterial, antiviral, and antifungal agents (Zhang et al. 2014). The structure of spirocyclic oxindolo- β -lactam or commercially known as chartelines is given in Fig. 1.

Zhang and coworkers reported that the construction of chartelines started from the bifunctional N-heterocyclic carbene undergoing Staudinger reaction of ketenes with isatin-derived ketimines. For such a highly complex compound, the %e.e reached up to 95 % with the yield of 89 %. Similar goes to the synthesis of γ -, δ -, and ϵ -chiral-1-alcoids, reported by Xu and coworkers (2014). The reaction was based on

both chemical and biological catalyses utilizing Zr for the carboalumination reaction and later applying lipase originated from *Pseudomonas cepacia* for the acetylation reaction. However, by comparing both types of reactions, biocatalysis has been known to provide better yield as well as %e.e (Tsai and Dordick 1996). One of the recent works in the development of pharmaceutically active compounds has been reported by Wen and colleagues where the group managed to synthesize (*S*)-propranolol through a coupled reaction with kinetic resolution as a recycling route utilizing *Candida antarctica* lipase B. The result showed an improve %e.e up to 100 % (Wen et al. 2014).

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Enantioselective Synthesis, Fig. 1 Chemical structure of spirocyclic oxindolo- β -lactam

Enantioselective Synthesis by Membrane Operations

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Enantioselective synthesis by membrane operations refers to chemical reactions to produce one enantiomer from a racemic mixture utilizing

membrane as a medium of separation. The process occurs in situ, where the product formed from the reaction will be directly separated into the required enantiomeric compound (Giorno et al. 1995; Long et al. 2005). Another enantiomeric synthesis, which applied the hollow-fiber membrane module, is from the work of Hadik and co-workers. The polymeric membrane made from polypropylene was used together with a chiral selector, N-3,5-dinitrobenzoyl-L-alanine octylester, initially dissolved in toluene (Hadik et al. 2002). Hollow-fiber membrane has also been applied with different types of chiral selectors for large-scale separation processes. The reported results suggested that N(1-naphthyl)-leucine provided a wide range of enantiomeric separation of amino acid derivatives with %ee of up to 95 % (Pirkle and Bowen 1994).

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Enantioselective Transport of Amino Acids by Membrane Operations

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Amino acids are molecules that contain an amino group ($-\text{NH}_2$), a carboxylic acid group ($-\text{COOH}$), and a side chain in each structure and

are the structural units of proteins. The most of amino acids found in nature are categorized as α -amino acid in which the amino group is attached to the carbon atom adjacent to the carboxylic acid group. An α -amino acid can exist in either of two optical isomers except glycine, and the isomer is normally described as L- or D-amino acid. The majority of amino acids in living organisms are L-isomers. Optical isomers, including amino acids, frequently show different bioactivity from each other. So, optical resolution of amino acids has been an important subject in various industries dealing with pharmaceuticals, foods, agrochemicals, and so on.

Optical resolution with membrane processes has potential merits over other separation methods like crystallization or chromatography. Membrane operation can be carried out continuously and it enables the large-scale separation. Optical resolution of amino acids can be achieved by the function of chiral recognition sites of solid membranes and liquid membranes. The method using liquid membranes is described in another site, so solid membranes for enantioselective separation are explained here. A main research topic on enantioselective membranes is the design of the membranes that have the chiral recognition sites. Some enantioselective solid membranes have been reported as follows.

Membranes Prepared from Chiral Polymers

Polypeptide and polysaccharide, like cellulose, alginate, and chitosan, and their derivatives are chiral polymers, and membranes from these chiral polymers have been applied to the enantioselective separation of racemic amino acids. The separation factor of these membranes toward racemic tryptophan is usually in the range of 1.1–5.0 (Higuchi et al. 2010). Membranes prepared from polymers with chiral branch have been also reported.

Membranes Added with Chiral Selectors

Enantioselective membranes can be prepared by the addition of chiral selectors that show

enantioselective affinity toward amino acids. Cyclodextrins, bovine serum albumin (BSA), and DNA have been used as chiral selectors. The membranes added with these chiral selectors showed the separation factor of 1.1–2.7 toward amino acids (Higuchi et al. 2010).

Molecular Imprinting Membranes (MIMs)

Molecular imprinting membranes are fabricated by incorporating the template molecules into the membranes and then removing the template molecules. The formed cavities in the membranes show the specific affinity with the template molecules and their analogue (Yoshikawa et al. 1995). Although MIMs currently show low enantioselectivity, this method has the potential of higher enantioselectivity (Xie et al. 2008).

Solid enantioselective membranes can be divided into two classes: diffusion-selective membranes and sorption-selective membranes (van der Ent et al. 2001; Xie et al. 2008). A diffusion-selective membrane is defined as a membrane with no specific chiral selectors for the chiral interaction but consists of a chiral polymer. Diffusion selectivity is caused by the chiral discrimination during diffusion. On the other hand, in a sorption-selective membrane, chiral selectors are embedded in a polymer matrix. To reach permeation selectivity in sorption-selective membranes, the selectively adsorbed population has to be mobile. An electrical potential is sometimes used for the purpose.

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Enantioselectivity

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Enantioselectivity is the preferential formation of a chemical reaction (mainly with metal complexes catalysts) of one enantiomer compound over the other (McNaught and Wilkinson 1997). The extent of enantiomeric reactions is determined by the percentage enantiomeric excess (% *e.e*) given by;

$$\% e.e = \frac{S - R}{S + R} \times 100$$

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Enantiospecificity

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Enantiospecificity is the ability of an enzyme to convert a racemic mixture into a particular enantiomer. The degree of specificity is interrelated with that of selectivity, which equation suggested by Lopez and coworkers (Lopez et al. 1990):

$$E_o = E^2 \left[\frac{\tanh(\Phi/E^{0.5})^{-1} - (E^{0.5}/\Phi)}{\tanh(\Phi)^{-1} - \Phi^{-1}} \right]^2$$

where

$$E = \frac{\ln[1 - c(1 + ee_p)]}{\ln[1 - c(1 - ee_p)]}$$

and

$$\Phi = \frac{v_{obs}}{D_{eff}S_o} \left(\frac{R}{3}\right)^2$$

and c is the conversion of the particular reaction (Tsai and Dordick 1996). If the calculated intrinsic enantioselectivity is extremely high, therefore, the reaction can be considered as enantiospecific.

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Encapsulation

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Synonyms

Encapsulation: [entrapping](#), [enclosing](#), [enveloping](#);
Amphiphilic substances: [Amphiphiles](#)

Definitions

Encapsulation: Coating or entrapping of active ingredient inside a solid shell or within a liquid or solid matrix of another material.

Complex coacervation: Coacervation caused by the interaction of two oppositely charged macromolecules.

Internal phase separation: Phase separation within emulsion droplets consisted of a mixture of polymer, good solvent and poor solvent, usually triggered by removal of good solvent.

Micelles: Spherical aggregates of surfactant molecules dispersed in an aqueous solution.

Liposomes: Spherical vesicles whose shells consist of single or multiple concentric bilayers resulting from the self-assembly of phospholipids in an aqueous solution.

Colloidosomes: Spherical vesicles whose shells consist of coagulated or fused colloid particles.

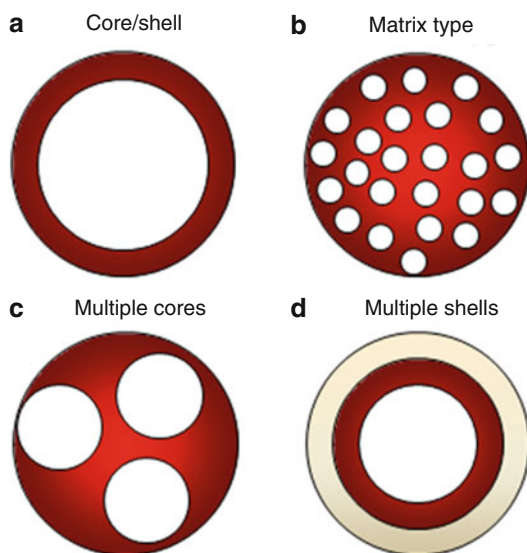
Polymersomes: Spherical vesicles whose shells consist of amphiphilic block copolymers.

Amphiphilic molecules: Surface active molecules made up of two parts, a polar or electrically charged hydrophilic part and a hydrophobic part, most often an alkyl chain.

Polycondensation: A polymerization in which the growth of polymer chains proceeds by condensation reactions between molecules of all degrees of polymerization.

Layer-by-layer polyelectrolyte deposition: A thin film fabrication technique based on depositing alternating layers of oppositely charged polyelectrolytes with wash steps in between.

Encapsulation is a process of enclosing or entrapping a core material (liquid, gas, solid particles, cells, dissolved active ingredients, etc.) inside a solid shell or within a solid or liquid matrix for the purpose of controlled or triggered release, immobilization, isolation, or protection of the encapsulated material. The material being encapsulated is called the core material, and the carrier material used for envelopment or entrapment is called the shell material. Typical examples of core materials are ink or dye for carbonless copy papers, liquid crystals for microparticle-based displays, phase-change material for smart textiles, high-molecular-weight gases for ultrasound contrast imaging, genetic material for in vitro compartmentalization, active food ingredients for functional food products, enzymes for biocatalytic reactors, drugs, pesticides, fragrances, antimicrobial agents, etc.



Encapsulation, Fig. 1 Schematic diagrams of capsules with different morphologies

Encapsulation efficiency (EE) is defined as the percentage of core material incorporated into the microcapsules relative to the total amount of the core material added during encapsulation process: $EE = (m_E/m_T) \cdot 100 \%$, where m_E is the mass of the core material incorporated and m_T is the total mass of the core material added. Loading capacity refers to the percentage of core material incorporated within the microcapsules relative to the total mass of the microcapsules (i.e., core + shell material).

Two main types of capsules can be distinguished, core/shell (reservoir) type and matrix type. In the core/shell capsule (Fig. 1a), the shell material completely surrounds and contains an internal core material (the internal phase). The strategies used for formation of shell are spray coating, complex coacervation, polymer precipitation by internal phase separation, interfacial reaction that may include polycondensation or cross-linking, and layer-by-layer polyelectrolyte deposition (Yow and Routh 2006). The core material can be released from core/shell capsules by simple molecular diffusion through the shell or by

deliberately compromising the integrity of the shell, e.g., by exposing the microcapsule to environmental stresses such as mechanical forces, change of pH, temperature, or ionic strength, or by chemical or biochemical degradation of the shell. A special class of core/shell capsules are micelles and vesicles (liposomes, polymersomes, and colloidosomes), formed by self-assembly of amphiphilic molecules (phospholipids and diblock copolymers) or particles (Dinsmore et al. 2002). Micelles are formed spontaneously when amphiphiles are dispersed in a polar solvent at concentrations that exceed a critical level, known as the “critical micelle concentration” (CMC). Micelles containing solubilized materials are referred to as microemulsions. A difference between micelles and vesicles is that vesicles are not a thermodynamically stable state of amphiphiles and do not form spontaneously, e.g., without input of external energy (Tadros 1993).

In the matrix-type capsule (Fig. 1b) the core material is distributed uniformly throughout a matrix of shell material. The most common release pattern from matrix-type capsules is first order in which the release rate decreases exponentially with time until the active ingredient is exhausted. Typical matrix-type capsules are multiple emulsions, hydrogel particles, solid lipid particles, polymeric particles, etc. Hybrid structures consisting of a number of hierarchically assembled homogenous phases may be engineered that allow for even finer control over the functionality of microcapsules (Fig. 1c, d).

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Encapsulation Application

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Synonyms

Bichromal particles synonym: Two-colored particles;
Microencapsulation synonym: Microentrapment

Definitions

Carbonless Copy Paper - Paper coated on the back side with colorless dye or ink capsules, that burst under the pressure of writing or typing and react with colorless clay particles coated on the upper surface of the second sheet.; Phase Change Material - A substance with a high heat of fusion that absorb or release a high amount of energy during melting or freezing, thus acting as a thermal energy storage; Electrophoretic display - a display that forms images by rearranging charged pigment particles with an applied electric field.

Microencapsulation can be done:

1. To protect the encapsulated material against oxidation or deactivation due to reactions with reactive species from the environment.
2. To mask the organoleptic properties like color, taste, and odor of the actives.
3. To achieve controlled/triggered/targeted release.
4. For safe handling of toxic materials.
5. To achieve in vitro compartmentalization or immobilization of biological materials and catalysts.

Microencapsulated materials are utilized in agriculture, pharmaceuticals, foods, cosmetics

and fragrances, textiles, paper, paints, coatings and adhesives, toner applications, and many other industries.

Carbonless copy paper developed by Green and Schleicher in the 1950s was the first commercial product to employ microcapsules. A coating of microencapsulated colorless ink is applied to the top sheet of the paper, and a developer is applied to the subsequent sheet. When pressure is applied by writing, the capsules break and the ink reacts with the developer to produce the dark color of the copy. Paper-like displays with low power consumption such as rotating bichromal microspheres system and microencapsulated electrophoretic system are other examples of commercial applications of microencapsulated ink (Yoshizawa 2004). In the rotating bichromal system (Gyricon), bichromal capsules with oppositely charged hemispheres are free to rotate within oil-filled cavities. In the microencapsulated electrophoretic display system (E ink), oppositely charged black and white particles move under an applied electric field in a clear liquid encapsulated within a transparent capsule.

Today's textile industry makes use of microencapsulated materials to enhance the properties of finished goods. One application increasingly utilized is the incorporation of microencapsulated phase change materials (PCMs), such as paraffin wax. Phase change materials absorb and release heat in response to changes in environmental temperatures. When temperatures rise, the phase change material melts, absorbing excess heat, and feels cool. Conversely, as temperatures fall, the PCM releases heat as it solidifies, and feels warm. Microencapsulation is also used in thermochromic and photochromic fabrics, which change color with changes in temperature or light, insect-repellent fabrics, which ward off mosquitoes, and scented fabrics, which release fragrance (Nelson 2002).

Pesticides are encapsulated to be released over time, allowing farmers to apply the pesticides less often rather than requiring very highly concentrated and perhaps toxic initial applications

followed by repeated applications to combat the loss of efficacy due to leaching, evaporation, and degradation.

Ingredients in foods are encapsulated for several reasons (Gouin 2004). Most flavorings are volatile; therefore, encapsulation of these components extends the shelf life of products by retaining the food flavors within that would otherwise evaporate out and be lost. Some ingredients are encapsulated to mask taste, such as nutrients added to fortify a product without compromising the product's intended taste. Alternatively, flavors are sometimes encapsulated to last longer, as in chewing gum. Some food ingredients must be encapsulated to be protected from oxidation or other degradation reactions caused by exposure to light, moisture, or oxygen. Microencapsulation preserves lactic acid bacteria, both starters and probiotics, in food and during the passage through the gastrointestinal tract, and may contribute to the development of new functional foods.

Many drug formulations for oral, intravenous, ocular, and subcutaneous administration are microencapsulated to achieve controlled, targeted, or triggered release of active ingredients. Aspirin, for example, can cause peptic ulcers and bleeding if doses are introduced all at once.

Microencapsulation of cells and enzymes is used to improve efficiency of bioreactors since very high volumetric productivity can be achieved; encapsulated biocatalysts typically have greater thermal and operational stability and downstream processing is simplified, since the encapsulated biocatalyst can easily be recovered and reused. In molecular biology, single-cell encapsulation is used to achieve high-throughput screening in directed evolution experiments.

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Encapsulation Efficiency

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The encapsulation efficiency (EE%) is defined by the concentration of the incorporated material (such as active ingredients, drugs, fragrances, proteins, pesticides, antimicrobial agents, etc.) detected in the formulation over the initial concentration used to make the formulation.

Encapsulation efficiency (EE %) was calculated using below formula:

$$EE \% = (W_t/W_i) \times 100\%$$

where W_t is the total amount of the incorporated material and W_i is the total quantity of incorporated material added initially during the preparation. W_t and W_i can be determined using spectroscopic or chromatographic method. If the capsule shell material is a polymer, it can be dissolved in the solvent, and the incorporated molecule will get soluble and it can be quantified. If the incorporated molecule is not soluble in that solvent, it can be extracted by adding the capsules in a liquid in which the target molecule is soluble (also by multiple extraction). If the core material is a liquid (such as emulsions), the amount of the encapsulated material can be evaluated after induced separation of the liquid dispersed phase and liquid continuous phase (i.e., simple emulsions) or in the outer liquid phase (i.e., W_2 in water-in-oil-in-water ($W_1/O/W_2$) emulsions). The amount of water retained within the oil droplets during emulsification is also significant for double emulsion. The methods used in this particular case enclose the measure of the outer water phase conductivity by differential scanning calorimetry (DSC) (Schuch et al. 2013).

The encapsulation efficiency can be influenced by (i) the partition coefficient of the target molecule in the solvents used in the preparation of the formulation, (ii) the method used to carry out the

encapsulation process (temperature, pH, mechanical stress), and (iii) the size distribution of the capsules (Jyothi et al. 2010).

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Encapsulation Techniques

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The encapsulation technique of choice depends on the type and physical properties of the core and shell material. The chosen encapsulation technique should give a high encapsulation efficiency and loading capacity of actives, capsules should not exhibit aggregation or adherence, capsules should have a narrow particle size distribution without tails, threads, or dents on the surface, and the process should be suitable for industrial scale production.

Depending on the initial physical state of the core phase, two different fabrication routes can be distinguished: (i) coating solid particles by shell-forming material in a fluidized bed or pan coater and (ii) dispersing a capsule-forming material in the form of droplets in another immiscible liquid or air, followed by droplet solidification. There is a variety of atomization and dripping processes by which a liquid phase can be dispersed in another immiscible fluid (Table 1).

Depending on the chemical composition of the shell-forming material, solidification of air suspended droplets can be achieved by solvent

Encapsulation Techniques, Table 1 Classification of dispersion techniques used in encapsulation processes

Liquid/air dispersion	Liquid/liquid dispersion
Atomization	Emulsification
Pressure nozzle	High pressure homogenizers
Two-fluid nozzle	Ultrasound homogenizers
Spinning disc	Static mixers
Dripping/jet breakup	Rotor/stator devices
Simple dripping	Microfluidic devices
Electrostatic extrusion	Membrane emulsification
Coaxial air/liquid flow	Microchannel emulsification
Jet cutting	Inkjet printing
Centrifugal nozzle	Micellization
Vibrating nozzle	

Encapsulation Techniques, Table 2 Common methods of solid shell/matrix formation in encapsulation processes

Mechanical/thermal	Physicochemical	Chemical
Cooling	Solvent removal	Suspension polymerization
Freezing	Evaporation or drying	One stage (direct) Two stage (droplet swelling)
Pan coating	Liquid extraction	Interfacial polycondensation
Fluidized bed coating	Layer-by-layer deposition	Sol-gel chemistry
Top spray	Self-assembly	
Bottom spray	Simple/complex coacervation	
Tangential spray	Ionotropic gelation	
Wurster process	Internal phase separation	

evaporation, cooling, or cross-linking in a hardening bath. Emulsification routes involve emulsification of a solution or suspension of actives, followed by shell/matrix formation by internal gelation, polymerization, layer-by-layer electrostatic deposition, internal phase separation, coacervation, etc. (Table 2).

Hydrogel capsules contain a hydrophilic active entrapped within a hydrophilic polymer network

that can absorb and hold large amount of water. A gel network can be formed by chemical gelation (polymerization by free radical processes or via condensation) or by physical gelation, which can involve heating (heat-setting gels), cooling (cold-setting gels), or the addition of multivalent counterions (ionotropic gelation). In the internal ionotropic gelation, the droplets of W/O emulsion contain a gel-forming polymer (e.g., alginate) and a cross-linking agent in a nondissociated form (e.g., calcium carbonate), whereas the continuous oil phase contains a species (e.g., hydrogen ions) that diffuses into the droplets and triggers the release of cross-linking agent in its active form and subsequent gelation. In the external ionotropic gelation, the droplets initially contain only a gel-forming polymer, and cross-linking occurs in a hardening bath (Zhang et al. 2007).

Coacervation involves the phase separation of one or more polymers from the initial solution and the subsequent deposition of the newly formed coacervate phase around the active ingredient suspended or emulsified in the same reaction media. In simple coacervation, phase separation is achieved by addition of desolvating agent (alcohol or salt) or by change in temperature or pH, whereas complex coacervation involves reaction between two oppositely charged polymers. The three basic steps in coacervation are (i) phase separation in a suspension or emulsion of active ingredient which leads to a three-phase system consisting of a polymer-rich liquid phase (coacervate phase), a polymer-lean liquid, and a solid or liquid phase containing active ingredient; (ii) deposition of the coacervate phase onto the dispersed particles or droplets; and (iii) hardening of the coating (Zuidam and Shimoni 2010).

Solid lipid microparticles contain the active ingredient entrapped within a high melting point lipid, such as fatty alcohols, fatty acids, fatty acid esters of glycerol, hydrogenated fatty acid esters, waxes, etc. Solid lipid microparticles can be fabricated by a temperature-controlled emulsification of high melting point lipids followed by cooling or by emulsification/solvent evaporation method. In the latter case, a high melting point lipid is dissolved in an organic solvent, and the mixture

is emulsified with an aqueous phase at room temperature. The solid particles are then formed by evaporation of the organic solvent. Hydrophilic actives can be encapsulated by forming a W/O/W emulsion prior to solvent evaporation or cooling (Jaspart et al. 2005).

Liposomes are usually prepared using two approaches: (i) hydration of dry lipid films with an aqueous solution of actives resulting in formation of large multilamellar vesicles (MLV), which is then followed by size reduction of MLVs by sonication, microfluidization, repetitive freezing and thawing, or extrusion through track-etch polycarbonate membranes, and (ii) mixing a nonaqueous lipid solution with an aqueous solution (Walde and Ichikawa 2001).

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Encapsulation: Entrapping, Enclosing, Enveloping

► Encapsulation

Engineered Organs

► Bioartificial Organs, Membrane Operations of

Engineered Organs and Tissue

► Bioartificial Organs and Tissue

Enhanced Oil Recovery (EOR)

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Enhanced oil recovery (EOR) aims at increasing the oil field's recovery yield, thanks to high-pressure injection of water or carbon dioxide. Injection of pressurized carbon dioxide leads to the maintenance of high pressures in the reservoir and to an improvement of oil displacement, thanks to several physical effects: decrease of oil viscosity due to carbon dioxide solubilization, stripping effects, and modification of multiphase equilibria due to CO₂ solubilization in the reservoir aqueous phase. When the oil reaches the surface, carbon dioxide is purged with the associated gas. Since the volumes of concerned carbon dioxide are very large – from 140 to 280 Nm³ par extracted barrel (Mazur and Chan 1982) – it is necessary to separate carbon dioxide from the

hydrocarbon gaseous phase in order to have it recycled to the reservoir (after pressurization).

Since the quantity of CO₂ dissolved in oil varies over a large range of values during the whole production of the reservoir (levels from 40 % up to 90 % can be observed after a few years of production (Cooley and Dethloff 1985)), it is rather difficult to design a cost-effective CO₂ removal unit that could operate during the entire life of the reservoir. Therefore, modular CO₂ removal units such as membrane operations offer much flexibility for such an operation (Table 1).

The first large-scale EOR project operating membranes has been carried out in the Sacroc oil field located in Western Texas. Carbon dioxide injection was launched in 1972 (at a flow range up to 240,000 Nm³/h). Three CO₂ recovery units were initially installed: two hot potassium carbonate-based absorption units (operated by Sun Explo with a 190,000 Nm³/h capacity leading to a reduction of carbon dioxide from 24 % to 0.5 % and Chevron, with a 54,000 Nm³/h lowering CO₂ content down to 1 %) and an amine (MEA)-based absorption unit (operated by Monsanto, with a 20,000 Nm³/h capacity). At the end of the 1970s, realizing that the level of CO₂ was raising at a higher rate than expected, Chevron contacted Cynara in order to install and operate two gas permeation units upstream of the hot potassium carbonate absorption columns. The

Enhanced Oil Recovery (EOR), Table 1 Comparison of relative investment costs (CAPEX) and operating costs (OPEX) of membrane-based, solvent-based, and hybrid processes for carbon dioxide capture (EOR applications)

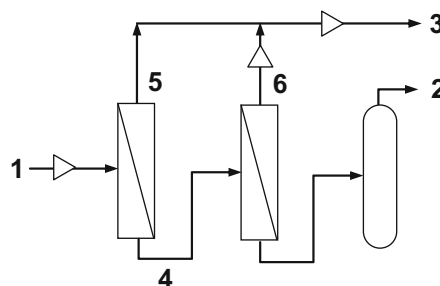
Operating conditions	Study realized by	Year	CAPEX réf.	Cryo. ^a	Mem.	Mem.	DEA	Cryo. ^a	TEA	KCO ₃ chaud
			OPEX réf.	+ Mem.		+DEA				
175.000 m ³ /h 90 % CO ₂ , 18 bar	Amoco (Goddin 1982)	1982	47 M\$			1	2.2	1.56	1.48	
			20.4 M\$/a			1	1.76	1.39	1.12	
118.000 m ³ /h 80 % CO ₂	Permea (Boustany et al. 1983)	1983	16.1 M\$	1.50		1				1.31
			6.5 M\$/a	1.31		1				1.82
190.000 m ³ /h 40 % CO ₂	Fluor Engineering Schendel and Seymour 1985)	1984			1				0.63	0.63 ^b
					1				0.56	0.68 ^b

^aCryo.: cryogenic distillation (Ryan-Holmes process (Kohl and Nielsen 1997))

^bHot potassium carbonate + membrane

Enhanced oil recovery (Kvaerner Membrane Systems)		1	2	3	4	5	6
Flow rate ($10^3 \text{ Nm}^3/\text{h}$)		26.5	7.4	18.9	11.2	15.3	3.8
Pressure (bar)		16	25	20	26	5	1
Composition (% mol.)	CO ₂	70	10	93.4	35.4	95.2	86.2
	CH ₄	9.6	26.9	2.9	20	2.0	6.7
	C ₂	6.3	10.0	1.0	14.0	0.7	2.4
	C ₃	5.6	18.4	0.6	12.9	0.4	1.5
	i-C ₄	2.5	8.6	-	6.0	-	0.2
	n-C ₄	1.3	4.3	-	3.0	-	0.1
	H ₂ S	0.6	0.01	0.8	0.1	0.9	0.4
	N ₂	4.1	11.8	1.1	8.6	0.7	2.5

CH₄ (C₂+) recovery yield = 77,8 % (73 %)



Enhanced Oil Recovery (EOR), Fig. 1 EOR example of permeation application (Spillman 1989)

treatment capacities of the membrane units were, respectively, 60,000 Nm^3/h at 35 bar feed pressure prior to the Sun unit and 25,000 Nm^3/h at 33 bar feed pressure prior to the Chevron unit. Cynara chose to operate a single-stage configuration, the membrane module being installed in parallel. The membrane operation proved to be highly flexible and reliable, as the membrane modules remained in operation twice longer than the expected lifetime (more than 5 years instead of 2–3 years) without any selectivity decrease. A slight decrease in membrane permeability has nevertheless been observed throughout the operation, and it was necessary to add more modules in order to maintain the production level of the membrane operation (Marquez and Hamaker 1986).

Since then, other membrane companies have seen their products involved in other EOR projects:

- Kvaerner membrane systems (Chapel et al. 1999):
Dallas Production Inc. (Texas) treated 200,000 Nm^3 of gases containing up to 25 % of carbon dioxide in 1994 during a feasibility study that lasted for 18 months. After this test, the membrane unit was in operation treating 1200 Nm^3/h .
Hydrocarbon Operating, Inc. (Texas) processed 590 Nm^3/h at 51 bar feed pressure in 1994 on a pilot skid composed of two tubular membrane modules.

– Medal:

A Medal membrane unit was operated at the need of the 1990s to process 14,200 Nm^3/h at 56 bar, 48 % CO₂, reducing the retentate CO₂ concentration down to 6 %.

– Cynara (Kohl and Nielsen 1995):

Amoco, Texas (1994): Cynara membranes were used to process 35,000 up to 120,000 Nm^3/h of gas containing 80 % CO₂.

Mobil, Salt Creek (1992): Cynara membranes were used to process 76,000 up to 120,000 Nm^3/h of containing 70 % CO₂.

Shell, Texas: Cynara membranes were used to process 13,000 Nm^3/h of gas containing 70 % CO₂ (Fig. 1).

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Environmentally Friendly Solvents and Diluents

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Non-solvent-induced phase separation (NIPS) and thermally induced phase separation (TIPS) are two major methods for polymeric porous membrane preparation. Solvents and diluents play important roles in NIPS and TIPS processes, respectively, influencing the final membrane properties during polymeric membrane formation. Applicable solvents for the NIPS process are N, N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), hexamethyl phosphoramide (HMPA), N-methyl pyrrolidone (NMP), tetramethylurea (TMU), triethyl phosphate (TEP), trimethyl phosphate (TMP), acetone (Ac), and tetrahydrofuran (THF), while applicable diluents for the TIPS process are dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), dihexyl phthalate (DHP), ethyl acetoacetate (EAA), propylene glycol carbonate (PGC), diphenyl ketone (DPK), diphenyl carbonate (DPC), cyclohexanone, camphor, and butyrolactone. Most of the above solvents/diluents are toxic, making the work atmosphere detrimental for workers and environment. Since

many membrane processes are employed with the objective of environmentally improving the process industry, toxic solvents/diluents reduce their contributions to environmental protection. Thus, finding more environmentally friendly solvents/diluents is becoming an important topic in the membrane preparation field (Cui et al. 2013a).

Recently, efforts have been done to develop environmentally friendly solvents for NIPS process and diluents for TIPS process. These solvents/diluents should yield the membranes' promising properties and performances without discharging toxicity to environment. It is much better if the solvents/diluents can be recovered easily. Dimethyl sulfoxide (DMSO) and glycerin triacetate (GTA), which can be employed for NIPS and TIPS process, are relatively less toxic. They have been used for polymeric membrane preparation. Acetyl tributyl citrate (ATBC) (Cui et al. 2013b), which is more environmentally friendly, was introduced to prepare poly(vinylidene fluoride) (PVDF) membranes via TIPS process. Dimethyl sulfone (DMSO₂) (Liang et al. 2013) was used as a universal crystallizable diluent to fabricate polar polymer membranes (PVDF, polyacrylonitrile (PAN) and cellulose acetate (CA)) via TIPS method. This diluent is easy to recover because of its crystallizable property. The membranes fabricated by above diluents presented promising mechanical properties and water permeability. Ionic liquid is a type of green solvents, which probably can be used for polymeric membrane preparations. CA membranes (Xing et al. 2010) have been formed via phase inversion employing 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) as the solvent and were recycled. The morphology, porosity, and pure water permeability of the CA membranes fabricated by reused solvents were quite comparable to the CA membranes produced by new solvents.

Researchers started to pay attention to develop environmentally friendly solvents/diluents, and preliminary progress has been made. However, this is far from the requirements, and more efforts are needed to contribute to this field.

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Environmentally Responsive Membranes

► Magnetically Responsive Membranes

Enzymatic (Peroxidase) Membrane Bioreactor

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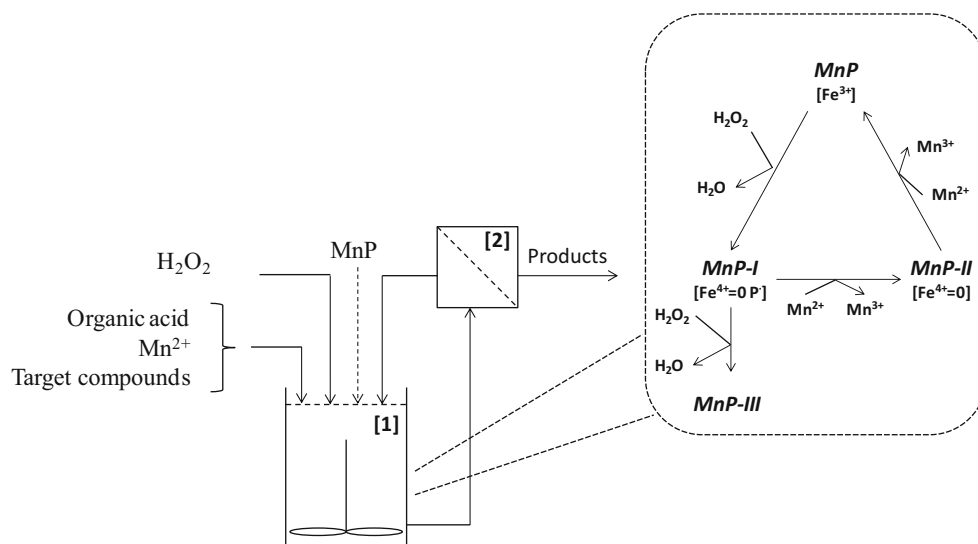
Enzymatic (peroxidase) membrane bioreactor is an enzymatic reactor coupled to a membrane in a number of configurations that allows the

separation of the enzyme and its reuse in the enzymatic process.

This technology is especially suitable in continuous operation by ensuring the recovery and reusability of the enzymes, allowing the minimization of large consumptions of biocatalyst. Various enzymatic membrane bioreactor configurations are possible, i.e., enzyme suspended in solution in a reactor connected with a membrane unit, immobilized enzyme within the membrane matrix itself, or entrapped enzyme in gel or microcapsules.

Among these setups, the retention of the enzyme by an ultrafiltration membrane is a very interesting alternative to overcome the washing out of the catalyst with the treated effluent but also to avoid the enzyme immobilization which is usually related with high costs, complex procedures, and loss of enzyme catalytic activity. In this system the enzyme is added into a reactor tank which is coupled with an ultrafiltration membrane to enable the retention of the free enzyme and its recycling back to the reaction vessel. Thereby, by using an enzymatic membrane reactor, it is possible to separate the biocatalyst from products and/or other substrates by a semipermeable membrane that creates a selective physical/chemical barrier (Fig. 1).

This type of bioreactor offers important benefits: high enzyme loads, prolonged enzyme activity, high flow rates, reduced energy requirements, straightforward operation, and scale-up, and also, fresh enzyme can be easily added to maintain constant enzymatic levels. Indeed, this system has been successfully operated for the continuous application of peroxidases (López et al. 2004) and laccases (Lloret et al. 2013). Specifically, peroxidase-based membrane bioreactors were applied for the transformation of various compounds with bioremediation purposes, for example, for the removal of dyes (Orange II) and estrogenic compounds (estrone, estradiol, ethinylestradiol, etc.). Orange II was successfully transformed by manganese peroxidase (MnP) in an enzymatic membrane bioreactor which consisted of a 250-mL stirred tank reactor (López et al. 2004 in Fig. 1) connected to a polyethersulfone synthetic membrane (Prep/



Enzymatic (Peroxidase) Membrane Bioreactor, Fig. 1 Scheme of an enzymatic (peroxidase) membrane reactor

Scale-TFF Millipore) with a molecular weight cutoff of 10 kDa (Lloret et al. 2013 in Fig. 1). Three stock solutions: H_2O_2 (94–312 mM); Mn^{2+} (33 μM), Orange II (0.1 g/L), and organic acid (1 mM); and MnP (7,000 U/L, 125–225 U/L in the tank), were fed into the bioreactor by independent variable speed peristaltic pumps, thus initiating the catalytic cycle of the enzyme. Under the best conditions evaluated, high decolorization yield can be achieved and minimal enzymatic deactivation, rendering an efficiency of 42.5 mg Orange II oxidized per unit consumed of MnP.

The findings obtained with the proposed reactor configuration allow its application as a novel treatment method for contaminated wastewaters. The simplicity of the operation, which mainly relies on the control of H_2O_2 dosage, promotes the peroxidase membrane bioreactor for further scale-up applications. The oxidative potential of the $\text{MnP-H}_2\text{O}_2\text{-Mn}^{2+}$ system appears to be general enough to be applied for the transformation of a wide range of compounds. The main requirement is that the oxidation potential of a particular substrate has to be lower than that provided by the enzymatic cycle, being the main factors affecting the stoichiometry and kinetics of the process the MnP activity, dosage rate of H_2O_2 , and concentration of the target compound.

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Enzymatic Membrane Reactor (EMR)

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Synonyms

[Enzyme membrane reactor](#)

A general definition of an enzyme membrane reactor (EMR) is a reactor system where a membrane separation is used to keep larger components in the reactor vessel (i.e., enzymes and/or

macromolecular substrates), while low-molecular-weight molecules (i.e., products and/or inhibitors) are allowed to pass freely through the membrane, thus leaving the reactor as permeate (Drioli and Giorno 1999). In this setup, several advantages of immobilized preparations, together with easy recovery of deactivated enzymes and replacement with fresh catalysts are achieved; inhibitors are continuously removed from the reaction vessel. The direct and deep contact between substrates and biocatalysts limits diffusional resistances, while no activity losses due to fixation to the support occur, thus maximizing the activity of the biocatalyst. On the other hand, enzyme stability is not improved.

Both dead-end and continuous stirred tank reactor (CSTR) ultrafiltration cells with flat membranes can be used as enzymatic reactors.

Performance of dead-end units is largely affected by the flow dynamics of the system; in fact, mixing of substrates and catalysts is not fully accomplished, and concentration polarization phenomena strongly limit reactor performance.

Continuous stirred tank reactors have been more widely adopted, both due to the possibility of concentration polarization control and easy modeling of enzyme kinetic behavior.

Assuming complete mixing within the reactor so that enzyme and substrate concentration in the reactor vessel are uniform, and the latter is equal to its value in the permeate, substrate mass balance in molar form can be written as:

$$(S_f - S)/\tau = R(S, P) \quad (1)$$

where

S_f = feed substrate concentration, ML^{-3}

S = substrate concentration, ML^{-3}

τ = reactor time constant, T

R = reaction rate, $\text{MT}^{-1} \text{L}^{-3}$

Product steady state mass balance similarly will be:

$$(P - P_f)/\tau = R(S, P) \quad (2)$$

where

P = product concentration, ML^{-3}

P_f = feed product concentration, ML^{-3}

Assuming that substrate conversion obeys the simple Michaelis-Menten model, substrate steady state mass balance reduces to:

$$XS_f + [X/(1 - X)]K'_M = K E V/Q \quad (3)$$

R being expressed as $K E S/(K'_M + S)$.

$X = (S_f - S)/S_f$ = conversion degree

K'_M = enzyme Michaelis-Menten constant, ML^{-3}

K = enzyme kinetic constant, T^{-1}

E = enzyme concentration, ML^{-3}

V = reaction volume, L^3

Q = flow rate, $\text{L}^3 \text{T}^{-1}$

The equation in this form is a useful tool to estimate parameters of reaction kinetics. Instead of performing nonlinear parameters estimation procedures, the functional dependence of XS_f on $X/(1 - X)$ can be plotted. The plot should look like a straight line whose slope is $(-K'_M)$ and whose intersection with the XS_f axis is given by the point of coordinate $(V_{\max}\tau)$.

Enzyme activity is usually not constant with time. Physicochemical changes in enzyme structure, thermal denaturation, and microbial contamination cause enzyme activity to continuously decrease with time. When enzymes or cells are compartmentalized in UF cells, biocatalyst losses can even occur due to the wrong choice of membrane molecular weight cutoff. It is conventional to measure the enzyme stability in terms of its half-life time ($t_{1/2}$), that is, the time at which enzyme activity is reduced to half its initial value. It can be calculated from the following equations:

$$K_d = \frac{2.303}{\vartheta} \log \frac{A_{E_0}}{A_{E_\vartheta}} t_{1/2} = \frac{0.693}{K_d} \quad (4)$$

K_d = enzyme deactivation constant, T^{-1}

ϑ = operation time, T

A_{E_0} = initial enzyme activity, or product mass per unit time and reaction volume, M T^{-1}

A_{E_ϑ} = enzyme activity at time ϑ , M T^{-1}

Since biotransformations by means of enzymes are continuous processes, as long as the reactor working life is longer than the native enzyme half-life, enzyme activity decay with time must be taken into account in order to correctly assess reactor performance. A transient substrate mass balance on the CST reactor leads to the equation

$$V[dS(t)/dt] = Q[S_f - S(t)] - V_{\max}V \quad (5)$$

where

V = reaction volume, L^3

S = substrate concentration, ML^{-3}

S_f = feed substrate concentration, ML^{-3}

$V_{\max}$ = enzyme reaction rate at saturating substrate concentration, $ML^{-3}T^{-1}$

Q = flow rate, L^3T^{-1}

Let us assume that substrate inlet concentration is much higher than the enzyme's apparent Michaelis constant, K_M' so that enzyme kinetics is expressed according to zero order kinetics, that is, $R = KE = V_{\max}$. Enzyme activity decay can be expressed in terms of the Arrhenius equation:

$$E = E_0 \exp(-K_d t) \quad (6)$$

where

E = enzyme concentration, ML^{-3}

E_0 = initial enzyme concentration, ML^{-3}

K_d = enzyme deactivation constant, T^{-1}

Equation 5 then takes the form

$$\begin{aligned} [S_f - S(t)]/\tau - dS(t)/dt \\ = V_{\max_0} \exp(-K_d t) \end{aligned} \quad (7)$$

Integration of the differential Equation 7 leads to estimate the outlet substrate concentration:

$$S(t) = \frac{V_{\max_0} [\exp(-t/\tau) - \exp(-K_d t)]}{(1/\tau - K_d) + S_f} \quad (8)$$

Estimation of the deactivation constant can be graphically carried out from Equation 7 plotting

$\ln\{[S_f - S(t)]/\tau - dS(t)/dt\}$ vs t . A straight line is thus obtained whose slope is given by $(-K_d)$ and the line intersects the vertical axis at the point of coordinate $(\ln V_{\max})$.

When the reacting solution is fed to the system, low-molecular-weight products leave the reactor permeating the membrane, whereas enzymes are partially or totally rejected. Then, enzymes tend to accumulate in a thin layer immediately upstream from the membrane causing polarization phenomena to occur. The extent to which concentration polarization affects reactor performance depends on the balance of rejected solutes, e.g., enzymes or cells, accumulation due to membrane rejection and back diffusion to the bulk phase, and eventually on the flow dynamics of the reacting vessel.

For macromolecules (like most biocatalysts), if membrane properties are carefully chosen, membrane rejection is usually very good, while biocatalyst back diffusion towards the bulk phase is extremely slow. The effect of concentration polarization on such reactor performances can then be significant.

Applying the thin film theory to a region immediately upstream from the membrane results in the following steady state mass balance equation:

$$JE = -D_e dE/dx \quad (9)$$

under the boundary condition (BC)

$x \rightarrow \infty E = E_s$

where

J = volumetric flux, $L^3L^{-2}T^{-1}$

E = enzyme concentration, ML^{-3}

E_s = enzyme concentration in the bulk liquid phase, ML^{-3}

D_e = enzyme diffusion coefficient, L^2T^{-1}

Under the assumption of totally rejected enzyme macromolecules, integration of Equation 9 allows one to express the ratio of enzyme concentration in the bulk solution in the presence of concentration polarization to its value in the absence of concentration polarization phenomena as:

$$E_s/E_o = 1/\{(1 - \alpha) + (\alpha/\beta)[\exp(\beta) - 1]\} \quad (10)$$

Enzyme concentration at the membrane–solution interface can thus be related to enzyme concentration in the bulk phase by the following equation:

$$E_w = E_s \exp(\beta) \quad (11)$$

where the dimensionless parameter β is a measure of convective mass transfer, J , relative to the overall mass transfer, D/δ , more generally K_s .

The change of enzyme bulk concentration can be dramatic, with changes in permeate flow rate, and applied pressure. Changes in enzyme bulk concentration may induce a large reduction in reaction rate within the membrane reactor. Under given stirring conditions, therefore, a critical value of flow rate and hence of applied pressure does exist. At flow rates lower than the critical value, the reactor always attains steady operation conditions, and correspondingly outlet product concentration is constant. Beyond the critical value, concentration polarization phenomena promote the localization of a large fraction of enzymes near the membrane surface, seldom leading to an enzymatic gel formation. Correspondingly, an accelerated deactivation of enzyme activity is superimposed on reactor performance thus hindering the attainment of steady state conditions. Experimental evidence suggests that the contribution of polarized enzymes to overall conversion can be negligible, due to the consistency of product concentration in the bulk phase of the reactor and in the permeate.

When macromolecular substrates are involved in the transformation under study, concentration polarization phenomena affect the EMR performance more severely. Diffusion limitations of macromolecular substrates hamper the use of immobilized enzymes in the hydrolysis of high-molecular-weight substrates. By selecting membranes with an appropriate molecular weight cutoff, both enzyme and substrate are retained in an EMR in touch with each other, and hydrolysis

products and/or inhibitors are continuously removed from the system. Soluble enzymes can then act directly on substrate macromolecules without diffusion limitations and steric hindrance imposed by enzyme fixation to a solid support. The stirring features of CST EMRs moreover assures that substrates and/or inhibitors within the reactor vessel are maintained at the lowest possible concentration level. Such reactor configuration is then extremely useful when substrate inhibited reaction patterns are involved or when inhibiting species are assumed to exist in the feed stream.

Diafiltration, semicontinuous, and continuous operational modes can be used.

Operating the reactor in a semicontinuous condition and adding substrate so as to keep its bulk concentration constant leads to meaningful changes in reactor performance as compared to the diafiltration mode. Under both operational mode, permeate flow rate continuously decreases with time.

When EMRs are operated continuously, feeding a slurry of substrate macromolecules to the reactor, concentration polarization phenomena play a dominant role. The presence within the reaction vessel of contaminants or intermediate products, which are not fully hydrolyzed by the enzymatic system under study can lead to membrane fouling or to the formation of a gel layer at the membrane surface. Under such conditions, the filtration rate continuously decreases with time, and it may happen that substrate conversion does not attain steady state conditions. The addition of enzymes capable of hydrolyzing such foulants to low-molecular-weight compounds usually improves reactor performance, eventually approaching steady state conditions in terms of both permeate flow rate and substrate conversion. In addition, antifouling procedures including suitable feed pretreatment or procedures to reduce concentration polarization can be used.

Equation 11 demonstrates the dependence of enzyme concentration at the upstream membrane surface on the flow dynamics of the reaction vessel. Due to the monotonicity of the exponential

function, at given applied pressure operational conditions improving mass transfer in the bulk phase (i.e., increasing axial flow rate improves K_S or D/δ) diminish concentration polarization. High stirring speeds usually improve filtering performance of a CST flat membrane reactor, albeit at the expense of partial enzyme deactivation.

Reactor configurations other than dead end or CSTR/UF cell can offer improvements.

The use of hollow fiber ultrafiltration modules in cross-flow filtration mode strongly improves both reactor performance and economics. Capillary membranes are characterized by a favorable surface to volume ratio; advantages from this feature are not only related to lower overall plant size but also to the increase of the surface to price ratio. Flushing enzyme/substrate solution through UF module tangentially to the membrane surface at a high linear velocity reduces the extent of concentration polarization avoiding the formation of a secondary enzymatic gel membrane. Provided that the volume of the UF module is small relative to the total volume, and that recirculation flow rate is much larger than permeate flux, system kinetic behavior can be modeled in terms of a CST reactor.

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Enzymatic Membrane Reactor in Supercritical CO₂

Gilbert M. Rios

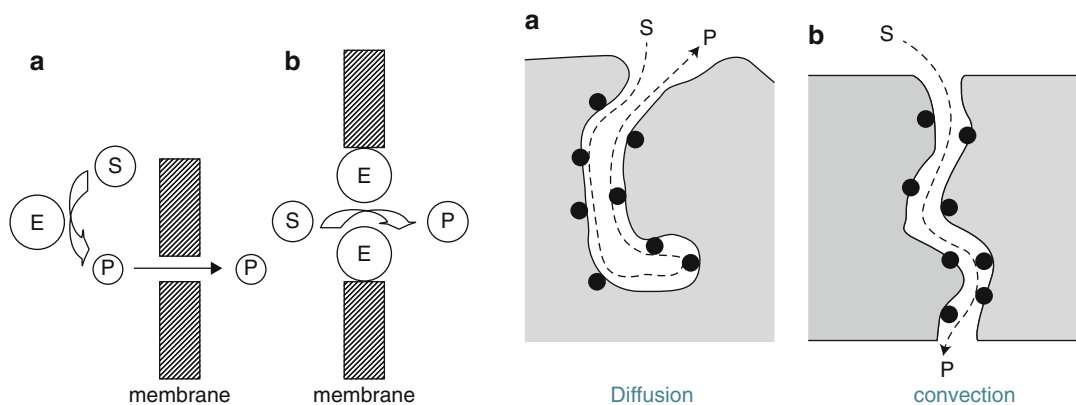
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Enzymes are catalysts obtained from nature (proteins), which work in mild conditions and

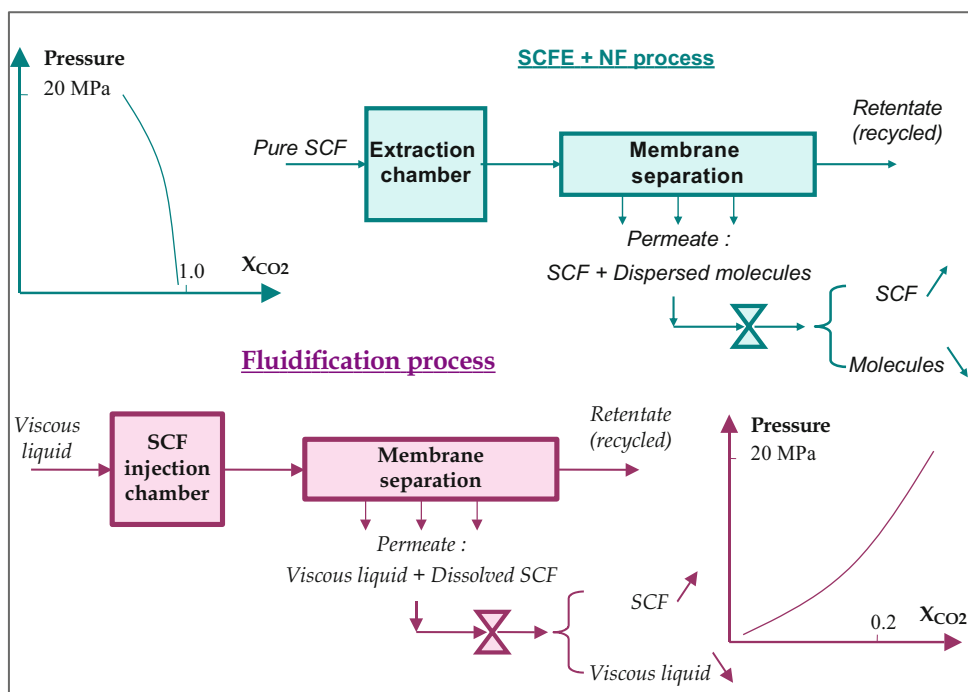
present very specific activities. They are one of the main tools of life as it developed since the origin. Enzymes are divided into six classes, based on the type of reaction that is catalyzed. Lipases are important enzymes that belong to the class of hydrolases; they catalyze hydrolytic reactions. *Candida antarctica* lipase B (CalB) is one of the most widely used lipases, because this enzyme accepts a broad spectrum of different substrates. Most of the time enzymes are immobilized for industrial applications. The main reason to immobilize enzymes lies in the reduction of costs by enabling efficient separation, recycling, and reuse of the expensive enzymes. The choice for the best immobilization method depends on the enzyme, the type of reaction, and the reaction environment.

The use of porous membrane reactor for enzymatic catalysis represents from this viewpoint a breakthrough technology which offers many advantages as compared to other more classical systems (immobilization on divided solid particles in fixed, fluidized, or moving beds): continuous mode, reduction of product/substrate inhibition, free enzyme end-products, and the possibility to set up monophasic or biphasic systems – even if there can be some drawback related to membrane fouling. The full activity may be maintained inside the reactor by the rejection of enzyme molecules (Fig. 1) either freely circulating (a) or immobilized on/in the membrane (b). In that case, the membrane is the catalyst media (functionalization) and the reaction occurs during membrane crossing. The convective control due to the application of a low transmembrane pressure (very small thickness of the porous layer: a few microns) is responsible for the mass transfer increase. The membrane is a macrosystem resulting from the assembly of swarms of microsystems: each pore represents a particular microreactor.

The main practical use of enzymatic catalysis in supercritical carbon dioxide (scCO₂) has to be found in producing high-added-value products since the process remains expensive. Lipases have proven to be rather stable and active during



Enzymatic Membrane Reactor in Supercritical CO₂, Fig. 1 Basic mechanisms



Enzymatic Membrane Reactor in Supercritical CO₂, Fig. 2 Plant schemas

long-term reactions in scCO₂. However, it cannot be stated that performing reactions in scCO₂ will always result in a higher activity. This is highly dependent on the type of reaction, the enzyme, and the applied conditions. The main advantage of CO₂, a very stable and nontoxic fluid, is therefore

the possibility of easier separation steps with complete removal of the solvent (Fig. 2).

The future perspectives for enzymatic membrane reactors in scCO₂ can be found in the combination of improving the stability and activity of the potentially interesting

enzymes – other types of enzymes are attractive for use in scCO_2 as well, such as oxygenases, epoxide hydrolases, aldolases, or decarboxylases – and an improved integration of the reaction and separation sections. Very interesting studies conducted lately on transesterification reactions with the fixed enzyme configuration (Fig. 1b), either using pure SC fluid solvent containing dissolved substrates or for transforming oils after the injection of a small quantity of pressurized CO_2 in order to decrease viscosity, are worth mentioning.

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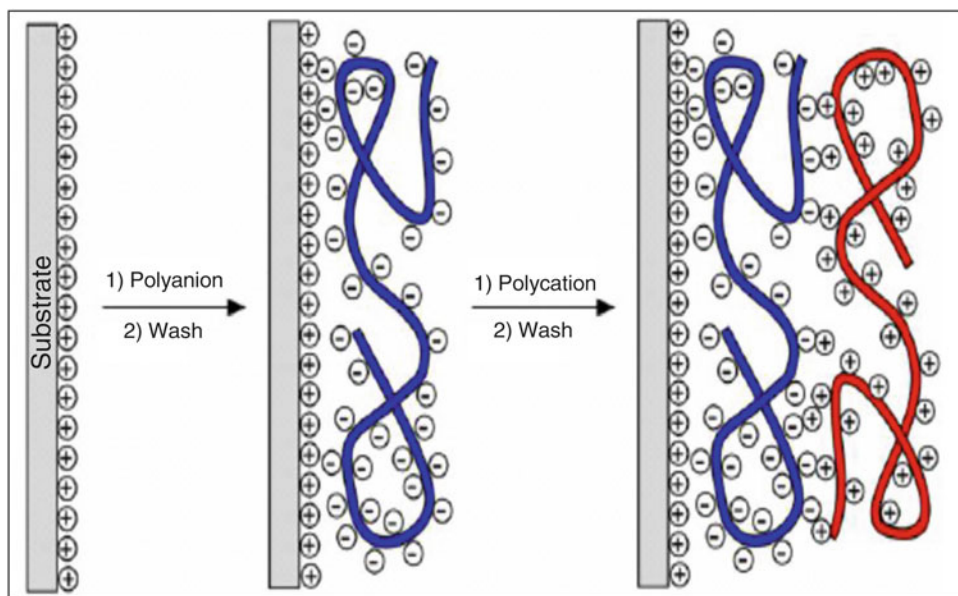
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Enzymatic Ultrafiltration Membranes (Immobilization of Urease and Trypsin)

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The sodium alginate was used as an anionic polyelectrolyte. The polyethyleneimine was used as a cationic polyelectrolyte. Trypsin (enzyme which catalyzed the hydrolysis of peptide bonds in which the carboxyl groups are contributed by the lysine and arginine residues) was applied as a positively charged polyelectrolyte and the urease (enzyme which catalyzes the hydrolysis of urea to ammonium and carbon dioxide) as a negatively charged polyelectrolyte. For adsorption of the polyelectrolyte layers, the supporting membrane (polyacrylonitrile-modified membrane negatively charged) was immersed in the solution of the cationic polyelectrolyte, rinsed with the buffer solution to remove excess of polycations on



Enzymatic Ultrafiltration Membranes (Immobilization of Urease and Trypsin), Fig. 1 Scheme of layer-by-layer adsorption of polyelectrolytes on membrane

membrane surface, immersed in the solution of the anionic polyelectrolyte, and rinsed with the buffer solution again. These steps were repeated to form multiple polyelectrolyte bilayers based on the electrostatic layer-by-layer self-assembly (Fig. 1).

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Enzyme Compartmentalization

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Synonyms

[Immobilization of enzymes](#)

In biology enzyme compartmentalization is efficiently carried out by biomembrane or biological membrane that permits to confine specific functions given by enzymes in a precise space. The enzymes can be localized inside the delimited compartments or on the membrane surface.

In eukaryotic cells the corresponding delimited spaces or compartments are called organelles, from which the main are the endoplasmic reticulum, Golgi apparatus, nucleus, mitochondria, lysosomes, endosomes, and peroxisomes. Each membrane-enclosed organelle contains a specific set of proteins free or on the membrane surface that regulates many vital biochemical processes. For instance, lipid metabolism is catalyzed mostly by membrane-bound enzymes.

Starting from nature simulation, in biotechnology process, enzyme compartmentalization can be obtained by immobilizing proteins on supports or delimiting them by support compartments. Membranes can be optimal supports for enzyme compartmentalization; in fact they are widely

used for the production of membrane bioreactors or biocatalytic membrane reactors (Mazzei et al. 2010). In particular, asymmetric hollow fiber membrane can be used as efficient support to compartmentalize enzymes by entrapment into the sponge membrane layer. The general membrane requirement is that the pores in the dense layer are small enough to retain enzyme molecules and at the same time large enough to freely pass substrates and products (Mazzei et al. 2013).

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Enzyme Membrane Reactor

- [Enzymatic Membrane Reactor \(EMR\)](#)

Enzyme Membrane Reactors

- [Membrane Bioreactors](#)

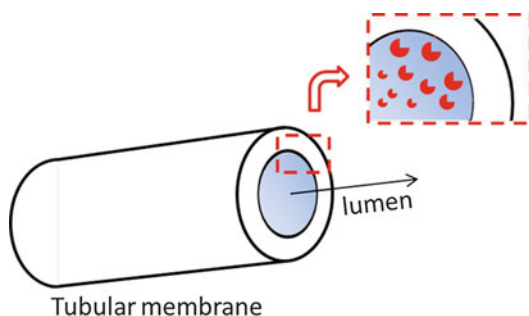
Enzymes Immobilized on Lumen

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Synonyms

[Immobilization of enzymes](#)



Enzymes Immobilized on Lumen, Fig. 1 Scheme of tubular biocatalytic membrane with biocatalyst immobilized on lumen surface

This particular kind of immobilization is generally referred to enzymes immobilized into the membrane lumen surface of tubular membranes for the production of biocatalytic membrane and biocatalytic membrane reactors. A scheme of a cross section of a biocatalytic asymmetric hollow fiber membrane is reported in Fig. 1, in which the place that the biocatalyst was immobilized on the membrane lumen surface is highlighted.

The biocatalyst can be also compartmentalized/segregated in the lumen of tubular membrane so confined in a defined region of the membrane module space. In these reactors, the enzymes or cells are not linked to the membrane. The membrane in this particular case can retain the enzyme or the cell which is not lost in the effluent stream, while low-molecular-weight products and inhibitors can be removed through the membrane (Strathmann et al. 2006).

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EOF

► [Electroosmosis, Overview of](#)

Ethanol Production by Continuous Fermentation-Pervaporation

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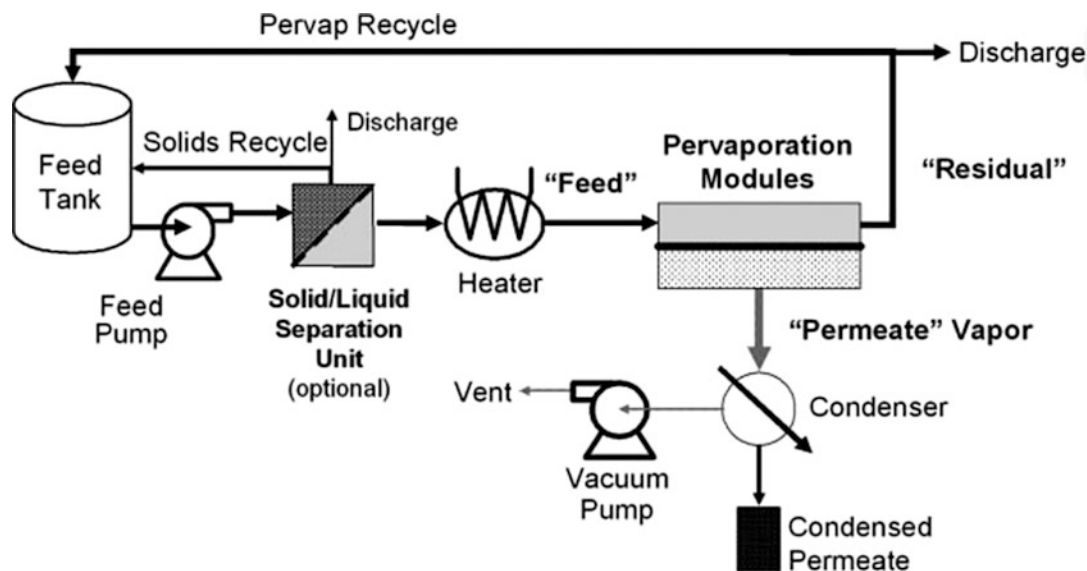
Ethanol production by continuous fermentation-pervaporation is a process that couples ethanol fermentation with in situ pervaporation (PV) recovery of ethanol from fermentation broth.

With the fast increasing of fossil fuel consumption and the deterioration of environment, it is commonly accepted that the fossil fuel for human energy use has to be replaced generally by renewable resources. Compared with traditional resources, bioethanol produced by fermentation process can be sustainably developed without extra yield of greenhouse gas (Peng et al. 2011). Bioethanol is produced from renewable resources (biomass) by ethanol fermentation process. However, usually, the maximum concentration of solvents (ethanol) does not exceed 8 wt% owing to the end-product inhibition on microorganism, resulting in high energy cost to separate ethanol from the dilute fermentation broth by distillation. Therefore, several in situ product-removal technologies, such as adsorption, gas stripping, liquid-liquid extraction, perstraction, pervaporation, and reverse osmosis, have been developed. These technologies could be coupled with ethanol fermentation process to decrease the effect of product inhibition and improve the sugar utilization and solvent productivity (Vane 2005).

Pervaporation coupled with fermentation, which is also called fermentation-pervaporation coupled process, has been regarded as the most promising separation method because this process

EOD

► [Electroosmotic Drag in Membranes](#)



Ethanol Production by Continuous Fermentation-Pervaporation, Fig. 1 Ethanol fermentation-pervaporation coupled process

can in situ extract organic components which is harmless for microorganisms in mild condition. Figure 1 shows its typical flow chart (Vane 2005). A pervaporation membrane module is connected to the fermentor to form a circulation of fermentation broth. Preheated fermentation solution is continuously circulated from fermentor through the membrane upstream side with another side being vacuumed using vacuum pump. Therefore, ethanol solvent can be selectively and continuously removed from the fermentation broth and then concentrated in the membrane downstream side. As a result, ethanol concentration in the broth is kept at low level to facilitate the continuous fermentation process as well as enhance the solvent productivity. In addition, a microfiltration/ultrafiltration unit can be alternatively installed before the pervaporation module, in order to filter microbes and avoid the biofouling of pervaporation membranes.

PV membranes can be made from either polymeric or inorganic materials, even both of them (Peng et al. 2011). The polymeric pervaporation membranes for extracting ethanol from fermentation broth include polydimethylsiloxane (PDMS) membranes, poly[1-(trimethylsilyl)-1-propyne]

(PTMSP) membranes, poly(ether block amide) (PEBA) membranes, liquid membranes, other modified polymer membranes, as well as porous polypropylene (PP) membranes and polytetrafluoroethylene (PTFE) membranes. Among them, the commonly used PDMS membranes with good selectivity and stability are regarded as the most potential PV membranes for ethanol recovery application (Xiangli et al. 2008). The typical inorganic membrane for PV is hydrophobic zeolite membrane, such as ZSM-5 and Silicalite-1 membrane.

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Ethanol–Water Mixtures: Separation by Pervaporation

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Pervaporation is an important membrane process in chemical industries in which valuables are isolated from the liquid mixture. Liquid and vapor separation by thermal processes has always been highly energy intensive, and new separation processes taking advantage of mass transfer through dense membranes have already shown they enable very significant energy savings as compared to more classic technologies (Anne et al. 2002). Membranes can be used for the selective removal of water from aqueous organic mixtures. Pervaporation (PV) is a separation process that involves separation of liquid mixtures, in contact with a membrane. With feed solution on one side, permeate is removed as a vapor from the other side (Brian et al. 2011); pervaporation (PV) is a very well-known membrane process for the separation of liquid and vapor mixtures due to its energetic aspects (EP 909209A1 1999; EP 944575A1 1999; EP 880400A1 1998).

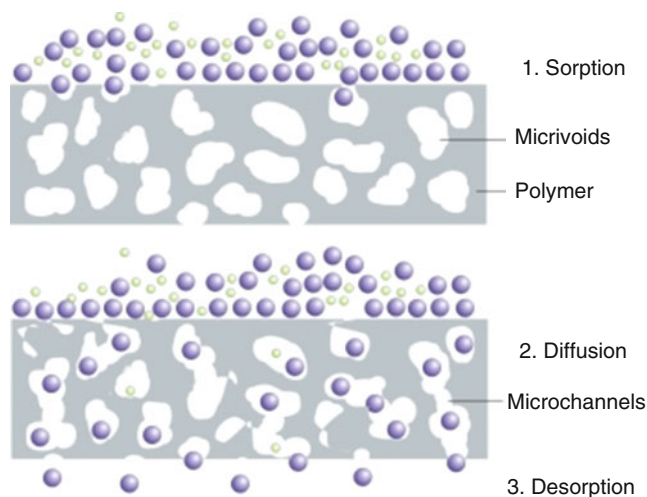
Pervaporation mostly allows a variety of possible application areas: dewatering of organic fluids like alcohols, ketones, ethers, etc. (EP 765682A1 1997); separation of mixtures from narrow boiling temperatures to constant (azeotrope) boiling temperatures (EP 811420A1 1997); removal of organic pollutants from water and air streams (EP 749351A1 1996); separation of fermentation products; and separation of organic-organic liquid mixtures (Kujawski 2000). Pervaporation is also considered as so-called clean technologies, especially well suited for the treatment and recycling of volatile organic compounds and pollution prevention (Anne et al. 2002).

Transport mechanism of PV through polymeric membranes was studied by many research groups, and it was explained by the solution-diffusion model (Binning et al. 1961; Paul and Paciotti 1975; Lee 1975; Mulder and Smolders 1984; Kataoka et al. 1991a, b). According to the solution-diffusion model, each component of the permeation molecules dissolves into the membrane and diffuses through the membrane due to the concentration gradient (Mikihiro et al. 1998) (Fig. 1).

Transport through the membrane is driven by the vapor pressure difference between the feed solution and the permeate vapor. The vapor pressure difference can be maintained by applying a vacuum on the permeate side or by cooling the

Ethanol–Water Mixtures: Separation by Pervaporation,

Fig. 1 Solution-diffusion mechanism (Graham 1866)



Ethanol–Water Mixtures: Separation by Pervaporation, Table 1 PV dehydration of ethanol through various polymeric membranes (Brian et al. 2011)

Polymer	Feed (wt% water)	Temp. (°C)	Separation factor	Flux (g/m ² h)
Regenerated cellulose	50	45	5.0	2060
Cellulose acetate	4	60	5.9	200
Teflon- <i>g</i> -polyvinylpyrrolidone	4	25	2.9	2200
Perfluorinated polymer on PAN support	1.3	50	387	1650
Nafion-H ⁺	4	70	2.5	5000
Polyacrylonitrile-polyvinylpyrrolidone	4	20	3.2	2200
Poly(maleimide- <i>co</i> -acrylonitrile)	15	15	33	8
Poly(acrylic acid- <i>co</i> -acrylonitrile)	18	15	877	13
Polystyrene	4	40	101	5
Poly(vinyl chloride)	4	40	63	3
Alginic acid	4	40	8.8	48
	5	60	13	2800
Chitosan	4	40	2208	4
Chitosan acetate salt	4	40	2556	2
Chitosan/glutaraldehyde	4	40	202	7
PVA/25 % TEOS, annealed at 160 °C	15	40	329	5
PVA/25 % TEOS, annealed at 130 °C	15	40	893	4

permeate vapor so that it condenses, thus creating a partial vacuum. Commercial systems for the dehydration of concentrated alcohol and other solutions have been developed since the 1980s, much of the push coming from interest in the production of pure ethanol as an alternative liquid fuel, where PV can be used to dehydrate (Brian et al. 2011).

Pervaporation Membranes

Polymeric Membranes

For dehydration, where the small molar volume favors the preferential sorption of water, materials have to be selected with a higher affinity for water than for the other component. The polymeric materials can be broadly classified into three categories: glassy polymers, rubbery or elastomeric polymers, and ionic polymers. In general, the glassy and ionic polymers are more suited for making water-selective membranes for dehydration.

For water-selective membranes, the most important factor responsible for the separation is the specific interaction between water and the polymer. To obtain high selectivities, it is

necessary to use polymers, which contain specific groups/active centers, capable of strong interactions with water.

The highest fluxes are those for the hydrophilic membranes based on cellulose and Nafion and grafts of hydrophilic poly(vinylpyrrolidone) on Teflon and polyacrylonitrile. The PVA/TEOS membranes are exceptions in that they are hydrophilic but exhibit low fluxes (Brian et al. 2011) (Table 1).

The emphasis is on selectivity, postulated to be determined by selective sorption and selective diffusion. Selective sorption is governed by the presence in the membrane of active centers such as charged sites which are capable of specific interaction with water, while selective diffusion is governed by the rigidity and regularity of the polymer structure and the nature of the polymer interspace, exemplified by the degree of swelling and the frequency of the cross-links. The results for a series of membranes made by grafting neutral or charged polymers onto supporting membranes are reported in (Table 2).

Polysalts, formed from anionic and cationic polyelectrolytes, would be appropriate for obtaining both highly permeable and highly selective membranes (Semenova et al. 1997) (Table 3).

Ethanol–Water Mixtures: Separation by Pervaporation, Table 2 PV dehydration of 20 % aqueous ethanol at 70 °C using graft polymer membrane having different charges (Brian et al. 2011)

Host polymer	Grafted polymer	Graft site charge	Separation factor
Polyvinylidene fluoride	4-Vinylpyridine	Neutral	9
Polyvinylidene fluoride	N-Vinyl-imidazole	Neutral	10
Polyvinyl fluoride	N-Vinylmethyl-acetamide	Neutral	4
Polyvinyl fluoride	N-Vinyl-pyrrolidone	Neutral	7
Polyacrylonitrile	Acrylic acid	Neutral	10
Polyacrylonitrile	K ⁺ acrylate	Anionic	500
Polyvinyl fluoride	K ⁺ acrylate	Anionic	156
Polyvinylidene fluoride	Quaternized 4-vinylpyridine	Cationic	175
Polyvinylidene fluoride	Quaternized N-vinylimidazole	Cationic	61
Polyvinylidene fluoride	4-Vinylpyridine/BrCH ₂ COOH	Zwitterionic	76
Polyvinyl fluoride	Vinylimidazole/BrCH ₂ COOH	Zwitterionic	63

Ethanol–Water Mixtures: Separation by Pervaporation, Table 3 PV dehydration of aqueous ethanol with membrane based on various polysalts (Brian et al. 2011)

Polyanion	Polycation	Feed (wt% water)	Temp. (°C)	Separation factor	Flux (g/m ² h)
Poly(acrylonitrile- <i>co</i> -acrylic acid)	Poly(acrylonitrile- <i>co</i> -vinyl pyridine)	10	—	5000	400
Cellulose-SO ₃ -Na ⁺	Polyethyleneimine	16	50	295	1900
Cellulose-SO ₃ -Na ⁺	PolyDADMAC, linear	16	50	140	3200
Cellulose-SO ₃ -Na ⁺	Same, but branched	16	50	123	4900
Cellulose-SO ₃ -Na ⁺	Poly-N, N-dimethyl-3, 5-dimethylenepiperidine chloride	16	50	123	2700
Aromatic polyamide sulphonate	Polyethyleneimine	20	60	15	300
Poly(acrylic acid)	Chitosan				
On polysulphone	supporting membrane	5	30	1008	132
No supporting	membrane	5	30	2216	33
Na ⁺ polystyrene sulphonate	Polyallylamine HCl	6.2	70	70	230
Na ⁺ CMC	Chitosan	10	70	1062	1140
Na ⁺ CMC	N-Ethyl-4-vinyl-pyridinium bromide	10	70	782	1320
Anionic PVA	Cationic PVA				
DS 2.3 %	DS 2.9 %	4.6	75	2250	378
DS 5.0 %	DS 5.2 %	4.6	75	1910	284

The best performers in terms of flux, which at a maximum of 5 kg/m²h never achieve high values, are charged polymers of one type or another, including polysalts. Anionic and polysalt membranes are superior. For anionic polymers, the proton form has a significantly higher flux than the metal or quaternary ammonium salt versions, owing to the greater free space within the polymer network (Table 4).

Hybrid Membranes

Many a times, the polymeric membranes may fail to meet the desired separation requirements. In such cases, it becomes necessary to add filler materials such as ceramics and zeolites to improve the separation properties of the membrane. There are several reports showing good separation performance for ethanol/water mixture using zeolite membranes (Kita et al. 1995; Sano et al. 1994).

Ethanol–Water Mixtures: Separation by Pervaporation, Table 4 Highest fluxes for PV dehydration of aqueous ethanol (Brian et al. 2011)

Membrane polymer	Mem. type	Feed (wt% water)	Temp. (°C)	Flux (g/m ² h)	Separation factor
Nafion-H ⁺	Anionic	4	70	5000	2.5
Cellulose-SO ₃ -Na ⁺ and polyDADMAC, branched	Polysalt	16	50	4900	125
K ⁺ acrylate graft on poly(vinyl fluoride)	Anionic	20	70	4700	156
PEI/PAA on RO membrane	Polysalt	10 ⁺	70	4050	1075
Cellulose-SO ₃ -Na ⁺ and polyDADMAC, linear	Polysalt	16	50	3200	140
K ⁺ acrylate graft on PAN	Anionic	20	70	3000	500

Ethanol–Water Mixtures: Separation by Pervaporation, Table 5 PV dehydration of ethanol using PVA/inorganic hybrid membranes (Brian et al. 2011)

Crosslinker	Feed (wt% water)	Temp. (°C)	Separation factor	Flux (g/m ² h)
TEOS (160 °C)	15	40	329	50
TEOS (130 °C)	15	40	893	40
PEG blend and TEOS	15	50	300	46
No PEG	15	50	160	500
Poly(acrylic acid) copolymer and TEOS	15	40	250	18
γ-Aminopropyl-triethoxysilane	5	50	537	36
Sulphated zirconia	5	50	263	10
	10	50	142	105
	20	50	86	183
	30	50	61	1036

Kita et al. made NaA-type zeolite membrane by hydrothermal synthesis. NaA zeolite membrane is a water-selective membrane, and the PV separation factor of water/ethanol system was over 10,000 at 348 K. For ethanol permselective membranes, Sano et al. (1994) prepared polycrystalline silicalite membrane by the hydrothermal synthesis.

The silicalite membrane showed high ethanol permselectivity, and a separation factor of 58 was realized at 333 K by PV. Silicalite membranes seem to have great potential for the ethanol recovery by PV (Table 5).

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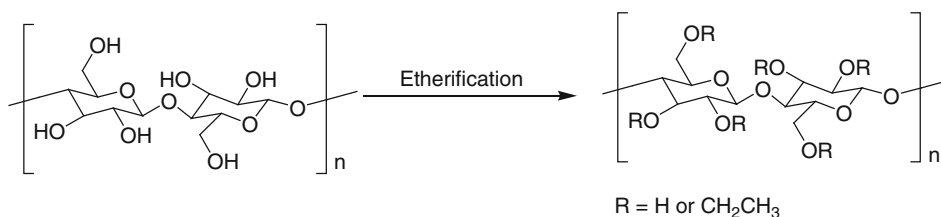
Ethyl Cellulose (EC) Membrane

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Ethyl cellulose (EC) membrane has mainly been used for separation of light gases, such as He, O₂, N₂, CH₄, CO₂, propane, and propylene. The hydroxyl groups on the glucose unit of cellulose

can be substituted with epoxy groups up to about 55 %, where ethyl cellulose exhibits good thin film-forming ability, excellent mechanical properties and durability, outstanding gas separation performance, and cost-effectiveness. Ethyl cellulose can be dissolved in organic solvents (e.g., chloroform) and ethyl cellulose thin film can be formed via solvent evaporation. The “nonporous” ethyl cellulose membrane has been used to separate light gases, where the solubility coefficient and the diffusion coefficient are two major parameters to determine the membrane performance for gas separation. This performance is also influenced by the content of epoxy groups, which vary with different manufacturers (Houde et al. 1997; Li et al. 2001; Ito et al. 1989) (Fig. 1).

Another important application of ethyl cellulose is in film coating of drug tablets. Although the tablet coating does not have a therapeutic value, it does offer the psychological importance in aiding patients to take the medication. The incorporation of color, flavor, and other additives in the ethyl cellulose-coated tablets can improve esthetic and organoleptic values and improve stability and handling capability and drug release properties. For example, ethyl cellulose is a water-insoluble polymer, which can be used to protect the hydrolysis of the drug by surface coating. The drug release rate can be adjusted by varying the thickness of the film and/or the composition of hydrophobic and hydrophilic components in the coating (Sakellariou et al. 1995). Similarly, ethyl cellulose can be used to formulate microcapsules where the target drug(s) can be tailored with controlled release rate, as well as improved efficacy, safety, processibility, and stability (Rogers et al. 2012). It is interesting to note that hydrophobic ethyl cellulose and hydroxypropyl cellulose, which is



Ethyl Cellulose (EC) Membrane, Fig. 1 Etherification of cellulose with maximum content of epoxy of about 55 %

more hydrophilic, are often combined together synergistically for varying biomedical applications (Donbrow et al. 1980).

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Ethylene Off-Gas

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Ethylene off-gas is a light gas mixture containing various concentrations of ethylene, propylene, hydrogen, methane, ethane, propane, and minor amounts of higher hydrocarbons, nitrogen, and other trace components.

The main ethylene-bearing off-gas streams are produced during the petroleum refining from fluid catalytic cracking (FCC) units and delayed cokers. FCC units alone produce significant amounts of ethylene and hydrogen, owing to the high feed flow rates processed. Other sources for ethylene off-gas streams are the deep catalytic cracking processes.

Refinery and petrochemical ethylene-containing off-gas streams usually contain varying amounts of heavy C_4 – C_{10} hydrocarbons, including alkanes, olefins, and aromatics, together with small quantities of water, nitrogen oxides, carbon monoxide, carbon dioxide, acetylene, methylacetylene, propadiene, butenes, and higher hydrocarbons. FCC off-gases are available at 10–17 bar and typically contain 8–18 vol.% of ethylene, 3–9 vol.% of propylene, and 12–20 vol.% of hydrogen, depending on the FCC feed composition and cracking severity (Netzer 2003). In general, ethylene-bearing off-gas streams contain relatively dilute concentrations of olefins, such as ethylene, with methane, ethane, and hydrogen which are potentially recoverable.

Hydrogen and light hydrocarbons (ethylene, propylene, and LPG) have an increasing worldwide demand. Being more valuable as chemical and plastic feedstocks than they are as fuels, the recovery from off-gas streams of these valuable compounds represents an interesting possibility to increase revenue in refineries (Hoffmann and Kaufmann 2012). Indeed, refinery and petrochemical ethylene off-gas streams are typically burnt in flare stacks or as fuel, since the recovery of the olefins by conventional means, such as fractionation, is considered as not economically viable. Considering the high cost of producing ethylene by thermal cracking of hydrocarbon feedstocks, which is the primary production process for ethylene, the recovery of olefins represents a substantial conservation of resources (Eldridge 1993). The available separation methods are absorption, adsorption, distillation, and membrane separation. Membrane technology represents a cost-effective, flexible, and safe process for recovering ethylene and associated hydrogen from refinery and petrochemical off-gas streams (Ohlrogge et al. 2010).

The use of a membrane system for vapor–gas separation allows valuable feedstocks to be recovered and recycled to the polymerization section in polyethylene and polypropylene production (Baker et al. 1998). Polyolefin plants involve present losses of monomers and other hydrocarbon feedstocks (typically \$1–\$3 million per year in one plant). Vent streams, containing monomer

contaminated with light gases (e.g., N_2 and H_2), are usually flared. Monomer recovery with hydrocarbon-selective rubbery membranes is the largest application of vapor separation membranes. The vent stream is compressed and cooled to condense hydrocarbons. The gas not condensed, still containing a significant amount of hydrocarbons, is sent to the membrane system and separated into a hydrocarbon-enriched stream as permeate and a nitrogen stream. The permeate is recycled to the compressor and then to the condenser where the hydrocarbon is recovered; the nitrogen stream is recycled to the degassing bin (Baker et al. 1998).

Analogous membrane processes are applied to recover ethylene in ethylene oxide and in vinyl acetate production. The purge gas for a typical ethylene oxide plant contains approximately 20–30 % ethylene, 10–12 vol.% argon, 1–10 vol.% carbon dioxide, 1–3 vol.% ethane, 50 vol.% methane, and 4–5 vol.% oxygen. A similar vent gas mixture is produced in the vinyl acetate process. A membrane recovery unit fed with these purge streams will produce an ethylene-enriched permeate stream and an argon-enriched residue stream (Jacobs and Billig 2005). These systems achieve an ethylene recovery greater than 70 %, partly recover methane (the diluent gas), and reduce hydrocarbon burning.

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Ethylene Production by Membrane Operations

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Ethylene (C_2H_4), also called ethene, is a colorless and flammable gas derived from natural gas and petroleum. Being particularly reactive, ethylene represents one of the largest volume compounds and a key building block in the petrochemical industry, with a worldwide demand that has grown steadily.

The conventional ethylene production process is steam cracking. A hydrocarbon feedstock (such as naphtha, liquefied petroleum gas, ethane, propane, or butane) is thermally cracked in the presence of steam, producing a mixture of hydrogen, methane, ethylene, ethane, and heavier components. Most of the dilution steam and heavier products are condensed by a rapid quenching, while the cooled gases are compressed, sent to a scrubbing for the acid gas removal, and subcooled for the successive separations. A distillation train performs the separation and purification of the gaseous products, representing an energy consuming step, highly heat integrated and requiring refrigeration (Ren et al. 2006). This provides a strong drive for evaluating alternative methods for separation and recovery purposes. Coke formation requires discontinuous operation for reactor cleanup. Different wastes are generated including caustic scrubber effluent, dilution steam condensate, coke and tar at the condensate separators, and vent gases generated during start-ups and shutdowns. Overall, this process is very capital intensive and energy consuming (Ren et al. 2006). This type of hydrocarbon feedstock affects the process capital cost as well as the amounts and types of waste streams. Cleaner and simplified processes are related to the use of ethane. Multiple companies are considering this option, driven by the large volumes of shale gas being recently recovered which provides sizable volumes of very low-cost ethane (Armor 2013).

The integration of membrane separation systems and of membrane contactors (such as membrane distillation, membrane strippers and scrubbers, etc.) and membrane reactors might beneficially contribute to redesign industrial operations. Indeed, membrane technology has many advantages over other conventional technologies, including lower capital and operating costs, low maintenance, low space requirements, flexibility, and ease of installation and operation (Strathmann 2011).

An ethylene production cycle by steam cracking was redesigned by integrating different membrane systems (► [gas separation](#) modules, ► [microfiltration](#), and membrane contactors) into a reference plant producing 800,000 t/year of ethylene and consuming ca. 30 GJ/t ethylene (Bernardo et al. 2004). Membrane gas separation to remove hydrogen from compressed gas allows a debottlenecking, reducing significantly the energy required in the cryogenic distillation for hydrogen/methane separation, permitting less severe operating conditions with respect to the conventional cycle (Engler and Dupuis 2000). Gas separation was also proposed to produce oxygen-enriched air to be used instead of air for combustion and/or decoking. Hydrocarbon removal from water streams using membrane contactors, capable to operate more efficiently with respect to conventional scrubbing units (Gaeta 2009), could achieve a removal greater than 90 %. Membrane contactors could be also applied for acid gas removal from the furnace effluent. Water used for scrubbing of the finest fraction of coke particles during decoking can be processed in a microfiltration membrane unit, recovering up to 90 % of the water and allowing its reuse in the plant. The replacement of traditional operations with membrane units, such as membrane contactors for washing water purification in the “hot section” and the membrane gas separation for the hydrogen recovery, determine a smaller exergetic loss with respect to the conventional industrial cycle (Bernardo et al. 2004).

Membrane reactors with inorganic membranes able to operate at high temperature were investigated for alternative ethylene productions, benefitting from the product continuous removal to shift a chemical equilibrium or from a reactant

continuous feeding to control the reaction selectivity. Some examples, related to the conversion of ethane, include the dehydrogenation by means of hydrogen permeable metallic membranes (Galuszka et al. 2008) and the exothermic oxidative dehydrogenation using perovskite membranes, which operate under a mixed ion-electron conduction (Lobera et al. 2011).

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Ethylene/Ethane Separation by Membranes

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The separation of ethylene from ethane and propylene from propane is a challenging operation. It is involved in the production of light olefins, such

as ethylene and propylene, which represent the most important building blocks in the petrochemical industry. Cryogenic distillation, conventionally applied to this separation, is highly energy intensive, requiring expensive tall columns, operated under low temperature and high pressure, with very high reflux ratios and requiring ethylene/propylene refrigeration systems for low-temperature cooling (Eldridge 1993).

Due to the complexity and difficulty of the separation process, mixtures including olefins produced in the petroleum and refining process are often used as fuel. Membrane separation, recognized as a low-energy method, appears the most promising among alternative separation techniques, such as extractive distillation, adsorption, and absorption, to recover these valuable compounds (Rungta et al. 2013). Polymeric membranes, cheap and with an easy processability, have low olefin/paraffin separation factor, especially those based on rubbery polymers (Rungta et al. 2013). The experimentally observed ethylene/ethane and propylene/propane upper bound, based on the most reliable data of various polymeric membranes, were presented in two critical reviews (Rungta et al. 2013; Burns and Koros 2003, respectively). Glassy polymers have been studied intensively for this separation. However, when applied to mixtures and/or at high gas activities, these materials are prone to plasticization which causes swelling of the polymer matrix and results in a higher permeability coupled with a loss of selectivity. Strategies to overcome plasticization include thermal curing and chemical cross-linking, which reduce the polymer free volume, and the addition of nanofillers (Goh et al. 2011; Ploegmakers et al. 2013).

Facilitated transport membranes based on the π -complexation mechanism are broadly investigated for olefin/paraffin separation (Faiz and Li 2012). The specific interaction between the hybrid molecular orbitals of the olefins and the atomic orbitals of the transition metals results in reversible chemical bonds stronger than those formed by van der Waals forces, but can be broken by simply increasing the temperature or decreasing the pressure. These systems allow high selectivity for the bound component. Silver-based facilitated

transport membranes were studied more extensively due to low-cost and relatively weak interactions with olefins (possible decomplexation). However, carrier poisoning and short life span of the polymeric membranes are typically reported (Rungta et al. 2013). Chitosan-based membranes, impregnated with silver nitrate as a facilitation agent, showed performance stability over thousands of hours of operation in field tests (Kamza et al. 2013). Ionic liquids, selected as additives for facilitated transport membranes, have a negligible vapor pressure that avoids solvent losses by evaporation and offer more affinity for the olefins compared to the paraffins, providing stability to the metallic cation dissolved inside and acting as a medium for facilitated transport with mobile carrier (Fallanza et al. 2013).

Carbon molecular sieve membranes showed the potential to surpass the polymeric ethylene/ethane upper bound performance (Rungta et al. 2013). These membranes are usually prepared by the pyrolysis of polymeric precursors such as polyimide materials. However, major issues are represented by their brittleness and poor mechanical strength.

In the field of inorganic membranes, metal organic frameworks were recently considered for preparing membranes to be applied to the olefin/paraffin separation (Bux et al. 2011).

The concept of hybrid processes, combining a membrane system with a conventional one, has drawn significant attention for the olefin/paraffin separation. Savings in total costs and energy (up to 30 %) could be obtained with a membrane/distillation hybrid system (Caballero et al. 2009).

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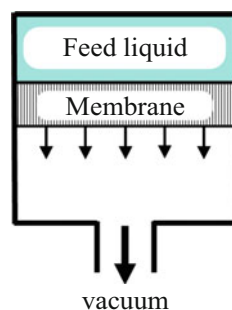
Evapomeation (EV)

Tadashi Uragami

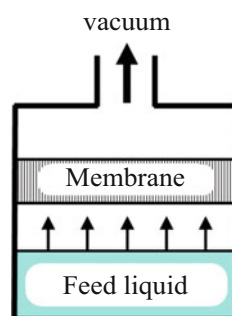
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Presently, pervaporation (PV) is applied as the chosen membrane separation technique for the separation of water/organic, organic/water, and organic/organic mixtures. However, it seems that conventional PV is not the most efficient membrane separation process for the treatment of some liquid mixtures as follows. Because the polymer membranes used in PV are directly in contact with the liquid feed solutions as shown in Fig. 1, however, specifically designed chemical and physical properties of the membrane are often impaired by swelling or shrinking of the membrane due to sorption of the feed components. Swelling or shrinking of the polymer membranes is disadvantageous for the membrane performance with respect to the separation of mixtures.

Evapomeation (EV),
Fig. 1 Principle of pervaporation (PV)



Evapomeation (EV),
Fig. 2 Principle of evapomeation (EV)



A novel membrane separation technique known as “evapomeation (EV)” (Uragami et al. 1988; Uragami and Saito 1989; Uragami 1991, 1992, 1993a, b; Uragami 1994; Uragami 1998, 2005, 2006a, b, 2008) makes use of the advantages of PV but reduces the negative effects of swelling on membrane performance. In this technique, the feed solution is fed to the membrane without directly contacting the polymer membrane. This is accomplished by vaporizing the liquid feed so that only vapor is supplied to the polymer membrane as shown in Fig. 2. Therefore, swelling or shrinking of the polymer membranes due to contact with the feed solutions is minimized.

The advantages of EV compared to PV are as follows:

1. In the EV process, membranes are not in direct contact with liquid feed mixtures as only vapors are supplied to the membranes. Accordingly, any swelling or shrinking of the membrane due to the feed mixtures is minimized, and consequently an improvement in membrane performance may be expected.

2. Because the organic liquid mixtures are vaporized, interactions between component molecules are significantly weakened, and consequently the separation performance is remarkably improved.
3. In EV, contaminants in a liquid feed mixture, such as macromolecular solutes, can lead to fouling of the membrane; this problem is avoided in EV.
4. During EV, both temperature of the feed solution and the membrane surroundings can be controlled; hence, an improvement in the permeation and separation characteristics of the membrane can be achieved.

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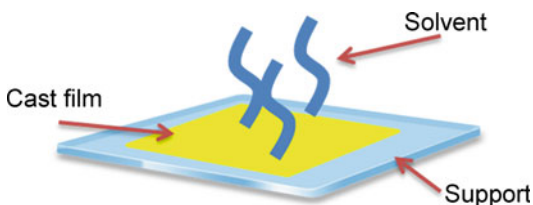
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Evaporation Casting

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Evaporation casting or dry-casting involves the evaporation of a solvent (or a mix of solvents) from a starting solution and the subsequent formation of a polymeric membrane by precipitation. In this process a polymer is dissolved in a suitable solvent and the solution obtained is spread out across an appropriate support. Then, the solvent is left to evaporate, in inert atmosphere or controlled environment, inducing the polymer precipitation and generating a membrane generally with a dense structure (Fig. 1). In evaporation casting, in fact, the precipitation process is much slower than the precipitation obtained by immersion casting. As a consequence, the membranes present, usually, an isotropic and less porous structure. Some other components, called commonly nonsolvents, can be also added to the initial polymeric solution. In this case, the solvent, the more



Evaporation Casting, Fig. 1 Evaporation casting process

volatile element of the system, will evaporate faster leading to a higher polymer/nonsolvent concentration responsible for the polymer precipitation. The evaporation process can proceed until the membrane has completely formed or it can be stopped by immersing the cast film in a coagulation bath containing a nonsolvent (Baker 2004). By prolonging or reducing the evaporation time before immersion in the coagulation bath, it is possible to tune the pore size of the membrane. When the starting polymeric solution is cast on different support, as porous thin films or other kinds of membranes, an asymmetric membrane with a dense skin layer deposited on a porous support can be obtained.

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Ex Situ Zeolite Synthesis

► Seeded Hydrothermal Synthesis for Zeolite Preparation

External Coagulant in Fiber Preparation

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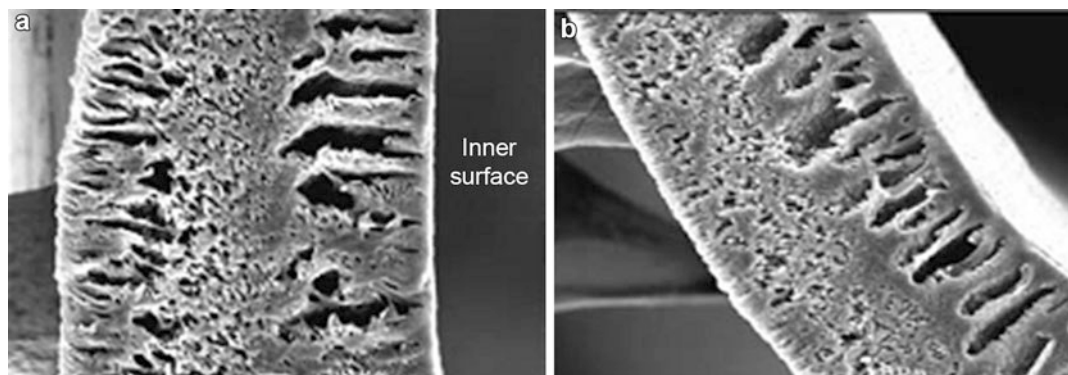
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External coagulant is a non-solvent liquid or a mixture of solvent/non-solvent in a collecting bath (coagulation bath) used for fabrication of fibers by the dry-/wet-spinning technique or the wet-spinning technique. Coagulation of the external surface of the nascent fiber can start immediately after its extrusion from the spinneret (wet spinning) or after the as-spun fiber crosses an air

gap (i.e., distance between the spinneret and the coagulation bath) through which the external surface experiences coalescence and orientation of polymer aggregates (wet/dry spinning). In general, the nascent fiber is partially coagulated by the internal coagulant (bore liquid) and/or through the air gap by solvent evaporation, and finally the coagulation is completed in the coagulation bath by an external coagulant.

The type of the external coagulant affects considerably the structural morphology of the resulted fiber. Usually, water is the preferred external coagulant because of its low cost and environmental friendliness. The proper choice of the coagulant is very important because the rate of demixing (i.e., phase separation) and the resultant inner and outer surface structures of the hollow fiber strongly depend on the chemistry and the composition of the coagulant. The molecular sizes and solubility parameters of the used solvent and the internal and the external coagulant play important roles on hollow fiber morphology. Solvent of a large size may have difficulties to leach out during the coagulation step. The difference in solubility parameters between the spinning dope solution and the bore liquid (internal coagulant) or the external coagulant affects the coagulation rate and subsequently the porosity of the spun hollow fiber membrane.

The interactions between solvent and external coagulant and between solvent and polymer play important roles affecting the rate of polymer precipitation. The temperature of the external coagulant affects also the polymer precipitation rate. The maximum amount of solvent that can be added to the non-solvent in the coagulation bath can be roughly determined by the position of the binodal (liquid-liquid boundary separating the miscible region from the immiscible one) in the ternary phase diagram presenting the composition of the polymer, solvent, and non-solvent. When the binodal shifts toward the polymer/solvent axis, more solvent can be added in the external coagulant. It is also possible to change from porous to nonporous external fiber surface by adding solvent to the coagulation bath (Mulder 1992). For example, when a strong coagulant such as water for poly(vinylidene fluoride),



External Coagulant in Fiber Preparation, Fig. 1 Cross-sectional scanning electron microscopy (SEM) structure of PVDF hollow fiber membranes prepared with different coagulants: (a) water coagulant;

(b) internal coagulant water and external coagulant 50 % ethanol in water (Reprinted from (Khayet et al. 2002). Copyright 2002, with kind permission from Elsevier)

PVDF, polymer is used for hollow fiber fabrication, a dense and smooth surface with no obvious pores is formed. However, when a weaker coagulant is employed such as methanol, which may be mixed with water, the roughness of the formed hollow fiber surface may increase considerably due partially to the formation of pores. These are the reasons for using the coagulants: 80 wt.% N-methylpyrrolidone (NMP) aqueous solution by Wang et al. (2008) for preparation of PVDF hollow fiber membranes and 80 wt.% methanol aqueous solution by Bonyadi and Chung (2007) for fabrication of dual hydrophilic/hydrophobic hollow fiber membranes for direct contact membrane distillation (DCMD) process. Figure 1 shows the effects of the external coagulant on the cross-sectional structure of porous hydrophobic hollow fiber membranes (Khayet et al. 2002). Water and 50 % (by volume) ethanol in water were used as internal and external coagulants. In Fig. 1a prepared with water as internal and external coagulants, long finger-like voids are formed near the inner surface, while smaller cavities are formed near the outer surface. Between the inner and outer layers, sponge-like structure appears. In Fig. 1b the outer layer is eliminated when ethanol is added to the external coagulant. The addition of ethanol delays the external coagulation process and the finger-like structure changes to a sponge-like structure. The slow coagulation of the hollow

fiber membranes can be explained on the basis of the mutual diffusivity of solvent/non-solvent exchange and solubility parameters of the materials involved in hollow fiber spinning. The addition of ethanol in water reduces the diffusion of non-solvent into the nascent hollow fiber membrane and consequently decreases the rate of precipitation. Khayet et al. (2002) observed an increase of the external surface roughness of PVDF hollow fibers when ethanol was added to the external coagulant and attributed the result to the increase of the pore size at the outer surface as ethanol was added in the coagulation bath.

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Extracellular Polymeric Substance (EPS)

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Extracellular polymeric substances or EPSs are biosynthetic polymers from prokaryotic (bacteria, archaea) and eukaryotic (algae, fungi) microorganisms, which either form (loose or tight) slimes around the microbial cells or are excreted as discrete gels to the surrounding environment. Typically, EPSs are heterogeneous mixtures of polysaccharides, proteins, nucleic acids, lipids, and other polymeric compounds. The highly diverse chemical composition of EPS is a result of the different processes related to their production and their immediate environment: active microbial secretion, shedding of cell surface materials, cell lysis, and adsorption from the environment (Wingender et al. 1999).

EPSs are often associated with the formation of biofilms and microbial aggregates. In biofilm systems, they are mainly responsible for binding cells and other particulate materials together and to the solid-liquid interface (Characklis and Wilderer 1989). In surface water sources, suspended EPSs are responsible for the formation of large aggregates of organic and inorganic suspended materials including living and dead microorganisms in the water (e.g., marine snow or mucilage). These aggregates are held together by a type of EPS mainly comprising of surface-active, algae-derived anionic polysaccharides collectively known as transparent exopolymer particles (Alldredge 2002). The latter has been recently identified as one of the major initiators of aquatic biofilms as it can form conditioning films on the solid-liquid interface conducive for bacterial attachment (Bar-Zeev et al. 2012).

Over the years, the important role of EPS in the microbial activities in natural aquatic systems is widely recognized. Moreover, it has also been identified to cause serious problems in technical systems ranging from the shipping industry,

power industry, microelectronics, and food industries to water purification (Flemming et al. 2009). In water supply systems, such problems are due to either organic or biological fouling of reservoirs, pipelines, media filters, and separation membranes.

EPS accumulation in membrane filtration systems can cause increase of operating pressure and cleaning frequency due to blockage of membrane pores as well congestion along the feed channel (Flemming et al. 1997). In NF/RO systems, it can directly cause decline in permeate water quality (e.g., salt rejection) due to hindered back diffusion of rejected salts and can indirectly cause membrane damage due to long exposure of cleaning chemicals and very high feed channel pressure drop (Vrouwenvelder et al. 2011). It has been proposed that the removal of planktonic EPS from the feedwater by pretreatment with dissolved air flotation (DAF) and/or UF/MF membranes can effectively minimize biofouling in NF/RO systems. However, this is still subject to extensive debate and investigations.

During algal blooms, very sticky EPS materials (including TEPs) produced by phytoplankton and bacterioplankton can cause physically irreversible (or non-backwashable) fouling in dead-end MF/UF systems (Villacorte et al. 2010). In this case, chemically enhanced backwashing (CEB) can be effective in restoring membrane permeability. However, applying an optimal dose of coagulant (conventional or in-line) prior to membrane filtration has been found to effectively minimize the need for chemical cleaning (e.g., Schurer et al. 2012).

Cross-References

► [Transparent Exopolymer Particle](#)

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Extracorporeal BALs

► Bioartificial Liver Support System (BLSS)

Extracorporeal Blood Oxygenation Devices, Membranes for

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Introduction to Extracorporeal Blood Oxygenation

In physiology, respiration is defined as the transport of oxygen from the outside air to the cells

within tissues and the transport of carbon dioxide in the opposite direction. The heart and lungs work together to ensure the circulation and the exchange of the respiratory gases. During circulation, the heart pumps oxygen-depleted blood to the lungs and then receives oxygen-enriched blood from the lungs for distribution to the rest of the body. In the lungs, the gas exchange process takes place in grapelike clusters of air sacs known as the alveoli. There are about 300 million alveoli in the lungs with a combined surface area of approximately 70 m². This is the area through which the blood–gas exchange takes place (Weibel 2009). Fresh air entering the lung carries oxygen with a partial pressure of oxygen (P_{O2}) of 160 mmHg; the presence of moisture in the lung alveoli results in reduction of the P_{O2} to 104 mmHg. The same air that enters the lung carries carbon dioxide with a partial pressure of carbon dioxide (P_{CO2}) of 0.3 mmHg. The carbon dioxide delivered to the lung from the blood in the venous ends of the pulmonary capillaries raises the P_{CO2} in the alveoli to 40 mmHg (McArdle et al. 2005). At the arterial ends of the pulmonary capillaries, oxygen diffuses from the air in the alveoli into the blood, and carbon dioxide diffuses from the blood into the alveoli because of differences in partial pressures. The heart then receives the oxygenated blood from the lungs and distributes it to tissues in the rest of the body. In most tissues, the P_{O2} is less than 40 mmHg and the P_{CO2} is greater than 45 mmHg so, because of the differences in partial pressures, oxygen diffuses out of the arterial ends of tissue capillaries into the cells, and carbon dioxide diffuses out of the cells into the blood. The heart pumps the oxygen-depleted blood back to the venous ends of the pulmonary capillaries entering the alveoli with a P_{O2} of 40 mmHg and P_{CO2} of 45 mmHg (Fox 2007).

In June of 2011, the World Health Organization classified heart diseases as the worldwide number one cause of death (WHO 2011). The treatment of many cardiac-related diseases such as coronary artery bypass grafting, valve repair, and aortic aneurysm repairs involves complex open-heart procedures where surgeons need to operate on a motionless heart in an almost

standard therapy for the treatment of respiratory failure in neonatal patients (Grenvik et al. 1999; Roy et al. 2000).

In adult and pediatric patients, clinical ECMO is a treatment of last resort for individuals who would otherwise die despite maximal therapy (Bartlett et al. 2000). Since the 1990s, this treatment has grown continuously in the treatment of adult patients with respiratory dysfunction, for oxygenation and carbon dioxide removal, and as a lung-protective ventilatory strategy in order to “rest” the lungs and provide optimal conditions for the recovery of lung function (Ghosh et al. 2009). Despite the current limited application of ECMO in adults, a randomized controlled trial (RCT) is recruiting patients in the United Kingdom to evaluate the cost-effectiveness and clinical benefit of modern ECMO technique (Peek et al. 2006). This RCT will be one of the first RCTs performed in adults since the benchmark NIH trial during the 1970s (Zapol et al. 1979) and could reveal an increase in the rate of survival of patients with severe, but potentially reversible, respiratory failure without severe outcomes of disability, if technical and clinical advancements improve outcomes.

Clinical Practice, Risks, and History of Extracorporeal Blood Oxygenation

Blood is a complex tissue designed to sustain the body by continuous circulation within a vast network of blood vessels coated with endothelial cells. These unique cells simultaneously maintain the fluidity of blood and ensure integrity of the vascular system. Contact with the surgical wound and diversion of blood into the heart–lung machine trigger a massive defense reaction that stimulates all types of blood cells and five plasma protein systems to produce a myriad of vasoactive cytotoxic and cell-signaling substances into the circulation. Platelets, neutrophils, monocytes, and endothelial cells are the major cellular actors, and complement, contact, intrinsic coagulation, extrinsic coagulation, and fibrinolytic protein systems are the primary plasma participants. When activated, these cells and proteins initiate complex and overlapping reactions and interactions with a multitude of target molecules to create a whole

body inflammatory response (Kirklin et al. 1983; Edmunds and Colman 2006). Although the safety of CPB has been established with low mortality rates, it is still associated to risks such as blood clots and air bubbles that can cause embolism (occlusion of a blood vessel), hemolysis or damage to red blood cells, and immune system activation or systemic inflammatory response. Studies show that presently patients undergoing cardiac surgery with CPB can still experience systemic inflammatory response syndrome (SIRS) (Segal et al. 1998; Onorati et al. 2010). This results in severe and irreversible effects such as cerebral injury and cognitive impairment (Lund et al. 2005), endothelial injury (Verrier and Boyle 1996), organ dysfunction and impaired hemostasis (Hsu 1997) also known as the process of blood clotting, blood coagulation or thrombus formation, graft occlusion, perioperative strokes and pulmonary thromboembolism (Valley et al. 2010), and even postoperative morbidity and mortality (Hammon 2008; Valley et al. 2010).

In order to prevent in-circuit thrombosis, or clotting, patients undergoing CPB or ECMO require the administration of systemic anticoagulation agents. Unfractionated heparin, which suppresses the action of thrombin, the key enzyme in the thrombotic portion of the defense reaction, has been the elected anticoagulant for over half a century. Although the results are generally satisfactory, there are sometimes controversial effects due to (i) thrombin being, in certain patients, only partially suppressed by heparin (Janvier et al. 1996; Edmunds and Colman 2006) or (ii) major hemorrhaging even after the patients are subjected to correction of the coagulopathy with antifibrinolytic drugs (Chalwin et al. 2008). About 30–70 % of patients undergoing coronary artery bypass grafting under CPB require homologous blood transfusions (Scott et al. 1992). The major risks such as SIRS, activation of the blood coagulation cascade, blood cell trauma, thrombosis, clotting, hemorrhaging, etc., which patients submitted to CPB and EMCO encounter, are all due to the contact of the blood with foreign surfaces of materials with inadequate blood compatibility also

known as hemocompatibility. Among these surfaces contacting blood in the extracorporeal blood oxygenation system, the membranes for the gas exchange are of primordial importance due to their extensive surface area.

The start of the historical development of extracorporeal circulation is strongly related to C sar Julian Jean Le Gallois (1770–1814). In the monograph published in 1812, *Experiences sur le principe de la vie*, he suggested that a part of the body might be preserved by a mechanical heart replacement and some kind of external perfusion device (Le Gallois 1812). After the first idea of external perfusion devices by Le Gallois, the first attempts of oxygenating blood outside the body were made by the physiologist Alexander Schmidt, in 1876, when he perfused an isolated dog kidney with oxygenated blood (Kramme 2011). The original BO, invented by von Frey and Gruber (Kay 1992), in 1885 was the film BO; it used rotating cylinders to spread blood in a continuously renewed thin film while oxygen flowed over it. Though there was direct contact between the blood and gas phases, the gas exchange efficiency was low, leading to devices that had very large priming volumes. Using the same principle, John Gibbon, best known for inventing the heart–lung machine, developed his first film BO in 1937 (Gibbon 1937) and, after years of tests and improvements, performed the first successful open-heart surgery with extracorporeal blood oxygenation in 1953 (Gibbon 1954; Edmunds 2004). After this, several forms of supplying oxygen to the blood were attempted, with more or less success, enabling the development of many models of oxygenators of which only a few were clinically employed such as the bubble BOs. In these devices, the gas exchange efficiency was increased by dispersing bubbles of oxygen directly into the blood, which resulted in significantly reduced priming volumes compared to the film BOs (Cahn and Li 1974). On the other hand, bubbling gas through blood led to foam formation, and therefore defoaming agents such as silicone compounds had to be added to the blood (Kremesec 1981). In 1955, DeWall et al. performed the first successful CPB procedure using a bubble BO (DeWall et al. 1966). The

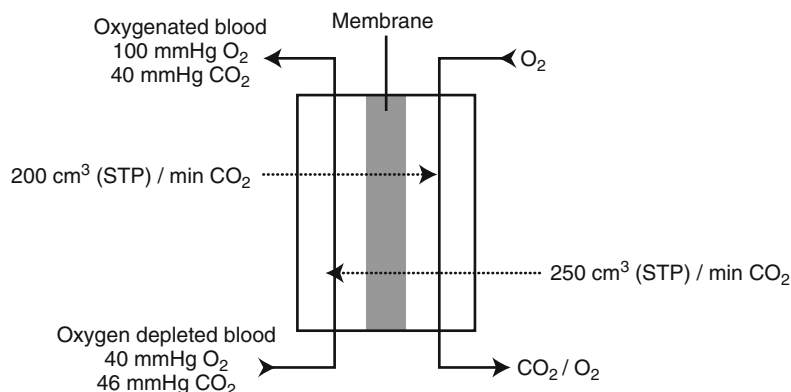
DeWall–Lillehei bubble oxygenator (Lillehei et al. 1955; DeWall et al. 1966) was a major breakthrough and well accepted by surgeons. It was a simple disposable device where oxygen bubbles were dispersed into an oxygenation chamber containing venous blood that was pumped from the patient’s body and then was defoamed in a defoaming compartment before returning to the patient. Although the benefits of bubble versus film BOs have been often debated, both have their own limitations. For film BOs, though the blood surface area was large, the gas transfer efficiency was often compromised by channeling of the blood flow (Niiya and Noble 1985; Ho and Sirkar 1992) and a very large priming volume was usually required to obtain sufficient gas exchange. On the other hand, bubble BOs caused significant damage to the blood due to the foam formation with devastating consequences such as denaturation of plasma proteins, gas emboli, fat emboli, fibrin emboli, and neurocognitive deficits (Lee et al. 1961, 1969; Hill et al. 1969). Despite the nonphysiological conditions of the blood–gas interface present in bubble oxygenators, these were used until 15 years ago in around 2–3 % of open-heart surgery worldwide (Wiese 2010).

Membrane Blood Oxygenators and Principle of Membrane Blood Oxygenation

Membrane blood oxygenators (MBOs) were first developed when the scientists introduced a nonporous symmetric membrane between the blood and gas phases to avoid direct contact between the two phases in an attempt to improve the hemocompatibility of BOs (Kolff and Balzer 1955; Clowes et al. 1956; Marx et al. 1962; Dorson et al. 1968; Guidoin et al. 1978). This represented a significant breakthrough in the development of blood oxygenation as the membrane provides a barrier in the blood–gas interface and that minimizes the risk of air embolism (Iwahashi et al. 2004). Microporous MBOs are, in fact, the state-of-the-art technology for extracorporeal blood oxygenation. Another advantage

Extracorporeal Blood Oxygenation Devices, Membranes for,

Fig. 2 The principle of membrane blood oxygenation



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of MBOs is in the device design and fabrication which, because of the defined blood channels, allows for precisely controlled blood flow characteristics and, therefore, possibilities for optimal efficiency in gas exchange.

As in the natural lungs, transport of gas into blood is driven by the partial pressure difference of the respiratory gases between the blood and the gas separated by the membrane. According to the pressure differences, gas diffuses through the membrane from the side of high partial pressure to the side of low partial pressure. Figure 2 schematically shows the principle of membrane blood oxygenation. In order to be clinically functional for an average healthy adult weighing around 70 kg, at rest, the MBO must deliver, at standard temperature and pressure conditions, approximately 250 mL of oxygen per minute and remove the corresponding carbon dioxide production of about 200 mL per minute. The controlling factor in the design of these blood–gas exchange devices is the permeability of the membranes toward oxygen and carbon dioxide. The equivalent oxygen partial pressure in venous blood is about 40 mmHg and about 104 mmHg for arterial blood. Use of air as the supply gas and at ambient pressure gives a driving force for oxygenation of about 88 mmHg. In contrast, in venous blood, the CO₂ partial pressure is about 45 mmHg which, assuming that the exchanging air has negligible CO₂ content, constitutes the maximum driving force for CO₂ removal from the blood. The initial challenge in membrane technology was to produce reliable membranes with high permeabilities for oxygen, and much

emphasis was placed on oxygen transfer as the controlling factor in the design of the blood–gas exchanger system. However, in some cases, removal of CO₂ from the blood may be a limiting factor in the design (Bungay et al. 1986; Stamatialis et al. 2008).

Development of Membrane Blood Oxygenators

The very first discovery of oxygen transfer across an artificial membrane was made by Kolff and Berk in 1944 when they found that venous blood was being oxygenated while flowing through a cellophane dialyzer that was in contact with oxygen containing dialysate (Kolff et al. 1944). This discovery stimulated the development of the use of gas permeable membranes in order to separate the blood phase from the gas phase in the BOs.

The first plate-type membrane oxygenator was built by Clowes Jr. in 1956 (Clowes et al. 1956). Clowes' membrane oxygenator was based on the Skeggs–Leonards (Skeggs et al. 1949; Skeggs 2000) plate dialyzer with its dialysis membrane replaced with a supported ethylcellulose flat sheet membrane. In order to have the sufficient oxygenating capacity for perfusion in an adult, it had to have a multilayered system with a very large membrane surface area of approximately 25 m².

In 1956, Kolff developed the first coil-type membrane oxygenator (Kolff et al. 1956b) by substituting the cellophane membrane in his own developed artificial kidney, the Kolff rotating

drum (Kolff 1954; Kolff et al. 1956a; Kolff and Watschinger 1956), with a nonporous symmetric dense polyethylene (PE) membrane. The blood flowed in a spiral mode, whereas the oxygen flowed parallel to the axis of the cylinder. To use this membrane oxygenator for an adult patient, it was necessary to assemble eight coil units with an enormous membrane surface area for effective gas exchange (Kolff et al. 1956a).

The second generation of nonporous symmetric membranes appeared in the 1960s with the development of silicone rubber which displayed increased oxygen and carbon dioxide permeabilities. The carbon dioxide permeability of silicone is about five times greater than the oxygen permeability, and this partially compensates for the smaller available driving force for carbon dioxide transfer (Haworth 2003). Since the diffusion coefficient of oxygen and carbon dioxide in air is about four orders of magnitude higher than in blood, the gas-side mass transfer resistance was negligible. The major resistance to respiratory gas transfer was due to the membrane and the blood-side concentration boundary layer (Weissman and Mockros 1969). This brought about a major advance in establishing the technical feasibility of membrane oxygenators in the 1960s and 1970s as the required membrane area could be optimized to less than 6 m^2 . Kolobow took advantage of the development of silicone rubber and in 1963 developed an oxygenator utilizing the same configuration of Kolff's coil lung but with a different assembly. A silicone rubber envelope reinforced with nylon knit was wrapped around a central core, and pure humidified oxygen was passed through it under a negative pressure. The blood flowed across the flat tubing parallel to the axis of the cylinder. The average priming volume of these units was of 0.1 L/m^2 , and they could oxygenate venous blood at rate of approximately $1 \text{ L/m}^2/\text{min}$ (Kolobow and Bowman 1963). In 1965, Bramson et al. commercialized the first disposable nonporous symmetric silicone MBO with an integrated heat exchanger (Bramson et al. 1965). In 1971, Kolobow (Kolobow et al. 1971) improved his first disposable coil membrane oxygenator by using membranes fabricated from silicone rubber deposited on a fabric

with an irregular structure. This membrane was originally manufactured by Fuji Systems in Tokyo, and its unique structure permitted enhanced secondary flow effects that improved the gas exchange capability. The improved Kolobow oxygenator was successfully used in the clinical field, first as an oxygenator for CPB during cardiac surgery, and later in respiratory assist devices was the only oxygenator available for long-term application of ECMO for acute respiratory failure patients (Kolobow et al. 1971). In 1972, J. P. Hill reported the first successful treatment of adult respiratory distress with ECMO (Hill 1977), and after 3 years of this success, the first neonatal ECMO survival case was described by R. H. Bartlett (Bartlett et al. 1976). This was the beginning of successful ECMO application, and it has been shown to be most effective in the treatment of newborn and pediatric patients (Bartlett et al. 1982).

The real breakthrough in MBOs came in the 1980s with the development of hydrophobic microporous membranes. These membranes were made from polytetrafluoroethylene (PTFE) and the membrane pore diameters ranged from 0.02 to $0.1 \mu\text{m}$. The respiratory gases pass through the membrane pores rather than diffuse through the membrane material and, consequently, offer a much lower resistance to gas transfer than the nonporous membranes. Polypropylene (PP) microporous membranes were introduced soon after and displaced the PTFE membranes because they have lower cost and better mechanical properties, which offered better control of the blood channel geometry (Haworth 2003).

In 1981, Y. Nose (Nosé and Malchesky 2000) started to work on the first microporous hollow fiber membrane oxygenator – the Monsanto oxygenator. Although the gas exchange characteristics were reasonable, the device leaked a large amount of plasma through the membrane walls. The first commercially available hollow fiber oxygenators, the Capiox MBO, composed of PP microporous membranes was developed in 1981 by Terumo Corporation (Terumo Corporation, Tokyo, Japan) and Suma (Suma et al. 1981). In order to avoid plasma leakage, the inner surface of the microporous PP hollow fibers was coated with

a silicone layer with a thickness of approximately 0.2 μm . In these two MBOs, the blood was pumped inside the bundle of hollow fibers (luminal flow), while the gases circulated on the outer side. As the venous blood entered each fiber, it was surrounded by an oxygen-rich ventilating gas mixture which passed through the fiber walls into the bloodstream (Weissman and Mockros 1968; Dutton et al. 1971; Suma et al. 1981; Tanishita et al. 1994). It was soon found that, for routine short-term perfusion, these types of MBOs presented no real advantage over bubble models mainly due to thrombus formation within the fibers (Calafiore et al. 1987; Bergdahl and Bergdahl 1989). In the 1980s, microporous MBOs with intraluminal flow accounted for only 20 % of all blood oxygenators sold in the United States (Voorhees and Brian 1996). At that time, the gas transfer performance of MBOs was not yet comparable with that of bubble blood oxygenators, and, furthermore, the MBOs were complex to operate.

The disadvantages presented by the MBOs triggered a series of studies on mass transfer efficiencies, pressure drops, and shear stresses through blood flow paths in different module configurations. Designers of flat sheet MBO modules focused on incorporating passive mixing of the blood to reduce the blood-side resistance to gas transfer, and in 1984, an oxygenator was introduced in the market by Cobe Cardiovascular (Cobe Cardiovascular, Arvada, Colorado), with a high gas transfer efficiency and a membrane surface area of only 2.5 m^2 . This was achieved through the introduction of spacers over the flat sheet microporous membranes to induce mixing on the blood side (Elgas and Gordon 1984). Extensive studies of MBO modules with hollow fiber intraluminal blood flow (Alpha et al. 1986; Gassman et al. 1987) led to the design of hollow fiber modules with blood flowing on the outside of the hollow fibers (extraluminal flow), while oxygen was administered through the inside of the membranes. In 1985, the Johnson and Johnson Extracorporeal Maxima Oxygenator (Johnson and Johnson Cardiovascular, Anaheim, California) was presented as a highly efficient and compact MBO. It contained microporous cross-wound

hollow fibers where the blood flowed over and under the outside of the fibers (extraluminal flow) while oxygen crossed from within the hollow fibers into the blood (Iatridis et al. 1985). In the 1980s, the Kuraray Corporation (Osaka, Japan) began on the development of a new device – the MENOX oxygenator – that contained a silicone-coated microporous polyolefin membrane. The reason behind the silicone coating is to reduce the plasma leakage through the membrane pores and to correct any defects at the surface of the membrane. The developers claim that the membranes are non-plasma-leaking and that the MENOX oxygenator could be used in ex vivo experiments for up to 5 months (Nosé 2001). Another coating developed by Medtronic Inc. (Minnesota, USA) comprised of an alkoxysilane/alkylsilane copolymer, preferably aminoalkylsiloxane, was used to coat microporous hollow fiber membrane blood oxygenators, increasing the resistance of the fibers to passage of blood plasma through the micropores (Plunkett 2002).

Nevertheless, in both cases, the coating provides an additional layer or “second skin” and introduces an additional barrier to the gas transfer, altering therefore a severe limiting factor of the oxygen mass transfer to the blood.

The technological advances of MBOs developed during the 1980s permitted the increase of the gas transfer efficiency and reduction of membrane surface area and priming volume. As a consequence of these improvements and with the general migration from blood flowing in the luminal to the extraluminal space of hollow fibers, by 1992, MBOs accounted for more than 98 % of all blood oxygenators sold in the United States.

State of the Art of Commercial Membrane Blood Oxygenators

The technical and medical progress of MBOs has been intrinsically associated to the development of membranes that can assure physiological transport rates of oxygen and carbon dioxide and of module configurations that are compact with minimal membrane surface area per unit volume and with low resistance to oxygen transfer, particularly on the blood side.

A membrane, in a very general sense, is a semipermeable barrier that can be made of inorganic or organic materials. In MBOs, organic polymers are the membrane materials of selection due to their physicochemical and structural versatility. According to their structure, membranes can be divided in four main categories: nonporous symmetric membranes, microporous membranes, integral asymmetric membranes, and composite asymmetric membranes. All of them can be processed in the form of flat sheets or hollow fibers (Bungay et al. 1986; Mulder 1996; Baker 2004). Nonporous symmetric membranes consist of a dense film where the selective transport of gases is governed by a solution/diffusion mechanism. Microporous membranes have a rigid, highly voided structure with randomly distributed, interconnected pores of different shapes and sizes from 0.01 to 10 μm in diameter depending on the preparation process. Asymmetric membranes, first developed by Loeb and Sourirajan in 1963 (Loeb 1981), consist of two layers: a dense and nonporous symmetric active “skin” layer with thickness ranging from 0.1 to 50 μm and a relatively thick porous support layer with thickness between 50 and 500 μm . The overall performance of the membrane is governed by the top dense layer, while the porous sublayer provides mechanical strength to the membrane. When the material of the top layer and porous sublayer are the same, the membrane is called an integral asymmetric membrane and when composed of different materials known as asymmetric composite membranes.

The packaging and arrangement of the membranes play a fundamental role in the development of MBOs. Efficient packaging of large surface areas of membrane into small volume devices lead to MBOs of high gas transfer rates and low priming volumes. Furthermore, the blood flow path must be carefully designed. While disrupting the blood-side mass transfer boundary layer will lead to higher gas transfer efficiencies, it also leads to increased shear stresses on the blood cells. Damage to blood cells depends both on the applied shear stress and on the time for which the shear stress is applied (Zydney 1985). Thus, while mixing on the blood side is desirable, it is essential

to ensure that the blood cells and blood components are not damaged.

Early microporous MBOs contained up to 5.5 m^2 of membrane surface area (Von Segesser 1987), so, in order to overcome slow gas transfer rates due to the high blood-side mass transfer resistance, modern MBOs have utilized secondary flow effects to disrupt the blood-side concentration boundary layer and hence reduce the membrane surface area and priming volume. In the case of flat sheet MBOs, such as the Cobe CML 30 (Cobe Cardiovascular, Arvada, Colorado, USA) (Voorhees and Brian 1996), the membrane surface area has been reduced to between 2.5 and 3.0 m^2 , whereas for hollow fiber designs with extraluminal blood flow such as the Cobe Optima (Medtronic Maxima, Medtronic, Anaheim, California, USA) (Ulrich 1990), the membrane surface has been reduced to between 1.7 and 2.3 m^2 .

In developed countries, the rate of growth of the elderly population is exceeding the growth rate of the rest of the population, and this means that in the near future cardiac surgery will be performed on older and less healthy patients, some of which may even need to undergo more than one operation (Voorhees and Brian 1996). This changing patient population as well as clinical and economic factors will demand improved MBOs. Designing improved and novel MBOs is a complex procedure given the interdependence of the important design variables as described below:

- Maximizing the gas transfer per unit priming volume of the device is essential. In the past, the patients’ body temperature was lowered by cooling the blood during CPB, thus reducing the oxygen requirement. In current practice, there is a trend toward normothermic coronary perfusion which increases the oxygen requirement (Galletti 1993). In addition, the need to minimize the transfusion of donated blood due to possible transmission of pathogens will drive module design toward lower priming volumes (Voorhees and Brian 1996).
- Minimizing the membrane surface area of the device has clinical and economic benefits. During CPB surgery, hematological and immune

responses are observed as a result of contact between the blood and oxygenator surfaces. While these side effects are relatively minor in healthy patients, they are of concern for older and less healthy patients. An increased gas transfer efficiency would allow a reduction in membrane surface area and hence a reduction in the average contact time between the blood and foreign surfaces. Since the membrane is often the most expensive component in a MBO, minimizing the membrane surface area will reduce manufacturing costs.

- The blood flow path must be carefully designed. While disrupting the blood-side mass transfer boundary layer will lead to higher gas transfer efficiencies, it also leads to increased shear stresses on the blood cells. Damage to blood cells depends both on the applied shear stress and the time for which the shear stress is applied (Kolff et al. 1944). Thus, while mixing on the blood side is desirable, it is essential to ensure that the cells are not damaged.

In the last decade, rather than focusing on the research of novel blood oxygenation membranes, most researchers have been concerned with blood flow configurations for mass transfer enhancement in hollow fiber MBOs. Extraluminal blood flow may be concurrent, crosscurrent, or counter-current to the flow of gas within the fibers, and all these flow patterns have been studied. Some researchers demonstrated that a hollow fiber module, in which the hollow fibers are perpendicular to the blood flow, is the most efficient as it promotes the disruption of the momentum and concentration boundary layer on the blood side. The subsequent decrease of the resistance to gas mass transfer leads therefore to the increase of oxygen transfer rates (Mockros and Leonard 1985; Yang and Cussler 1986, 1986; Rajasubramanian et al. 1997; Wickramasinghe and Han 2005). However, this blood flow arrangement complicates the design of oxygenators because of the complex blood flow path and the non-applicability of conventional mass transfer correlations. As a consequence, many studies of momentum and mass transfer in MBOs have been

carried out (Vaslef et al. 1994; Gabelman and Hwang 1999; Wickramasinghe and Han 2002; Taskin et al. 2010). Nagase et al. (2005a, b) have thoroughly investigated the relationship between the oxygen transfer rate and hollow fiber arrangement and found better mass transfer performance in parallel flow hollow fibers. This was due to the fact that in the hollow fiber module with blood perpendicular flow, the hollow fibers in the front layer conceal those in the rear layer at the cross-over point, and this decreases the mass transfer rates. Furthermore, the membrane surface areas of these parallel modules were larger than the ones in the other modules. Other studies show that high gas transfer rates can be obtained when microporous hollow fiber membranes are arranged in an orderly way in cross-laid double layer mats at an optimal membrane angle (Catapano et al. 2001).

The MBOs used in ECMO for long-term lung support system applications in infants and adults account for a very small part of the MBOs used worldwide. The flat sheet coil-type modules are generally composed of a nonporous, dense flat sheet reinforced silicone rubber membrane envelope in a spiral coil around a polycarbonate spool. The blood flows between turns of the envelope in a thin film, and oxygen from the gas compartment diffuses through the membrane into the bloodstream. At the same time, carbon dioxide diffuses through the membrane into the gas compartment and is flushed from the oxygenator by the oxygen flow. More recent oxygenators aimed for long-term ECMO usage are based on hollow fiber silicone-based membranes with extraluminal blood flow (Kawahito et al. 2002a, b; Motomura et al. 2003).

Hollow fiber and flat sheet MBOs have almost equivalent hemocompatibility and gas exchange performance. However, the gross air handling is different due to differences in the packing density defined by the total available membrane surface area per unit volume. Gu et al. (2000) compared flat sheet and hollow fiber MBOs in terms of pressure drop, shear stress, and activation of leukocytes or white blood cells. They found that both configurations displayed similar gas transfer performance. However, the pressure drop along the blood flow path of the flat sheet MBOs was higher

than that for hollow fiber MBOs. Moreover, activation of leukocytes in flat sheet MBOs was greater. De Somer et al. (1996) compared flat sheet and hollow fiber MBOs in terms of hemolysis, shear stress, and white blood cell and platelet counts and found that although they have important differences in pressure drop and shear stress, no statistical differences were found in hemolysis generation or other tormented blood elements. Therefore, pressure drop as a single element may not be considered to influence hemocompatibility.

A tremendous amount of research, as evidenced by the numerous scientific articles and patents, has been devoted to the design of the MBOs available today. In 1999, the total BO market was worth about \$460 million and by 2001 had risen to over \$500 million (Hanft 2002). In 2008, an estimated 1.4 million MBOs were used worldwide for acute surgical CPB, corresponding to a consumption of approximately 3 million km² of oxygenation membranes (Wiese 2009).

Presently, most of the MBOs sold worldwide contain hydrophobic microporous membranes, and more than 95 % of them are composed of extraluminal flow microporous hollow fiber membranes with pore sizes below 0.1 μm , outer diameters between 300 and 500 μm , and surface areas of approximately 2 m². The hollow fiber membranes are assembled into carefully spaced cross-laid double layer woven mats which provide uniform extraluminal flow channels for the blood (Hanft 2002). The main polymers used in the production of the blood oxygenation membranes are polyolefins such as polypropylene (PP), polyethylene (PE), and poly-4-methylpentene (PMP) and, at a smaller scale, polyvinylidene fluoride (PVDF) and silicone rubber (Wiese 2009).

Current Problems

Extracorporeal membrane blood oxygenators (MBOs) used in the medical field to substitute the respiratory function of the lung have at their very core membranes that act as a blood–gas barrier and ensure oxygen delivery and carbon dioxide removal from the patient’s bloodstream.

In order to be technologically feasible, the MBOs, with minimal membrane surface area, have to comply with two main properties: (i) be efficient gas exchangers and provide physiological oxygen and carbon dioxide transfer rates of approximately 250 cm³ per minute and 200 cm³ per minute, respectively, at standard temperature and pressure conditions and (ii) be hemocompatible.

The majority of current MBOs are made of hollow fibers of microporous hydrophobic materials with pore sizes below 0.1 μm . The resistance of these membranes toward the respiratory gases is very low as the gas exchange between the blood side and the gas side is performed by diffusion and convection of oxygen and carbon dioxide via the open pores. MBOs with these types of membranes have high gas permeabilities and are routinely used to provide temporary cardiopulmonary bypass (CPB) during open-heart surgery and are also occasionally used for extracorporeal life support (ECLS) to substitute short-term cardiopulmonary function in patients with respiratory failure. One of the drawbacks of microporous hydrophobic membranes is plasma breakthrough which occurs when plasma protein layers are formed at the membrane surface and grow through the membrane pores increasing the surface energy of the pore, allowing plasma to leak through from the blood side to the gas side (Montoya et al. 1992).

Another main concern that has troubled the membrane industry for the past 30 years and to date remains a serious issue is the blood compatibility or hemocompatibility of the oxygenation membranes. The definition of biocompatibility has been updated for over 20 years and can be considered as being the body’s acceptance of the material, i.e., the ability of an implant surface to interact with the cells and fluids of the biological system and to cause exactly the reactions which the analogous body tissue would bring about (Ratner 1993; Williams 2008). Presently, the biomaterials community has been unable to more accurately assign the term “blood compatible” to a given biomaterial in spite of 50 years of intensive research on the subject. There is no clear consensus as to which materials are “blood compatible” as blood material interactions are complex and involve multiple factors including

surface chemical composition, charge, flexibility, wettability, and conditions of blood flow (Cazenave 1987). Furthermore, unlike biocompatibility assays, there are no standardized methods to assess blood compatibility (Ratner 2007). Labarre's (2010) tentative definition of a blood compatible surface is "a surface able to keep under control coagulation and inflammation processes at its interface with normal blood, in given hemodynamic conditions." According to Ratner, we still do not have truly blood compatible surfaces after 60 years of intense research of blood compatibility and after numerous approaches have been tried (Ratner 2007). The hemocompatibility of biomaterials is known to be dependent on various surface properties such as surface morphology, surface chemical composition, surface charge, surface wettability, and surface topography. The overall blood-contacting surfaces must avoid damage to the blood cells and components but also to avoid stagnation and localized clotting.

To improve blood compatibility of transport surfaces such as the ones in MBOs, researchers have focused mainly on surface modification techniques and producing hemocompatible surface coatings. Minimization of blood/material interactions can be achieved through chemical modification; however, these methods are still far from perfect. Surface chemical modification, besides requiring rather complex experimental procedures and involving high costs, still does not offer surfaces with long-term stability and leads to potential complications downstream (Klee and Höcker 2000). Most manufacturers have focused on the development of anticoagulant-based coatings for the entire bypass circuit including the oxygenation membranes. This approach led to the commercialization of microporous-coated membranes and bypass-coated circuits. Various manufacturers claim that the added layer of material provides a blood-surface interaction with improved hemocompatibility compared to that seen for the bulk fiber materials. For example, heparin is known to have good blood compatibility properties and has been used as a coating on several commercialized products. Unfortunately,

heparin-based coatings are inherently expensive and complex due to the use of sodium heparin, a complex, costly, and fragile biologically derived substance. The Carmeda Bioactive Surface (Medtronic, Inc.) uses a polymer primer coat followed by covalent attachment of heparin to primary amino groups present in the primer coat (Stenach et al. 1992; Spiess et al. 1998). The Duraflo Bonded Heparin Surface (Baxter, Inc.) uses a heparin-polymer blend-based coating that is intended to achieve similar results (Toomasian et al. 1988; Mottaghy et al. 1989). Other heparin-based coatings intended to improve blood compatibility are available from other medical device manufacturers such as Terumo (Fukasawa 1983), 3M Sarns (Zacour 1988; Fried and Bell-Thomson 1992), etc.

Despite these developments, in order to prevent in-circuit thrombosis, or clotting, when subjected to extracorporeal blood oxygenation using any of the MBOs available on the market, patients still require the administration of anticoagulant drugs that often lead to major hemorrhaging and blood transfusions.

Another approach to improve the hemocompatibility of membranes destined for MBOs focuses on the development of novel blood oxygenation membranes made from materials different to the polyolefins mentioned before. Polyurethanes (PUs) first found a niche in biomedical applications mainly because of their unique mechanical properties, particularly fatigue resistance, tensile strength, and abrasion (Szycher and Poirier 1983; Szycher et al. 1983; Graig 1983; Gogolewski 1989; Hepburn 1992; Furukawa 1997), but also because of their good bio- and hemocompatibility properties (Boretos 1980; Wang and Cooper 1983; Yoon and Ratner 1988; Gogolewski 1989). PU membranes are a good candidate for blood oxygenation devices as the type, length, ratio, and crystallinity of the different monomers as well as the method of membrane preparation determine the bulk properties responsible for the final mass transfer properties (Yilgör and Yilgör 1999; Hoshi et al. 2000; Jonquière et al. 2002) and the surface properties that affect bio- and hemocompatibility (Yoon and Ratner 1988; Gogolewski 1989).

Blood Compatibility and Membrane/Blood Interfaces

In 2007, an estimated 250 million polymeric devices contacting the bloodstream were used in humans. All of these blood-contacting devices exhibited thrombosis problems, and all cardiovascular device procedures, both short term and long term, required significant anticoagulation, at high cost and with considerable risk to the patient (Geckeler et al. 1997). The number of blood-contacting medical devices used worldwide is increasing every day, but their hemocompatibility properties still remain far from ideal.

To this date, there is no consensus definition of blood compatibility. In 2007, Buddy Ratner labeled as a “catastrophe” the fact that the scientific community has still not been able to accurately assign the term “blood compatible” to a biomaterial in spite of 50 years of intensive research on the subject (Geckeler et al. 1997; Ratner 2007). While the definition of biocompatibility is generally accepted as the ability of a material to perform with an appropriate host response in a specific application (Williams 1987), blood compatibility or hemocompatibility has received different definitions by various authors. From a clinical point of view, a biomaterial can be considered as blood compatible when its interaction with blood does not provoke either any damage of blood cells or any change in the structure of plasma proteins. Only in this case can it be concluded that this material fulfills the main requests of biocompatibility (Gurland 1987). A tentative definition, by Labarre (2010), of a blood compatible surface is “a surface able to keep under control coagulation and inflammation processes at its interface with normal blood, in given hemodynamic conditions.”

The contact between the blood and the surface of a biomaterial often leads to different degrees of clot formation, as a consequence of the nonspecific protein adsorption and adhesion and activation of blood cells (Horbett 1986; Courtney et al. 1994). Within the first few seconds after blood contacts, material surface plasma proteins are deposited. The extent of protein adsorption depends on the properties of the foreign surface, namely, the wettability, charge, roughness,

chemical composition, etc. This protein layer controls further reactions of the other blood components and cell system. Additionally, the adsorbed proteins are subject to conformational changes as well as exchange processes with other proteins (Ziats et al. 1988). The competitive adsorption behavior of proteins at the material surface determines the pathway and the extent of intrinsic coagulation and adhesion of platelets. Platelets play a fundamental role in hemostasis. Following the protein adhesion to the surface of the biomaterial, coagulation is initiated by platelets adhering to specific binding sites exposed by the plasma proteins. The activated platelets swell, grow spiky extensions known as pseudopodia, and release the contents of their secretory granules, which contain a variety of substances which include ADP, serotonin, and thromboxane A₂, which stimulate further platelet adhesion and activation and enhance the coagulation process. A large variety of clotting factors take part in a series of chemical reactions that eventually create a mesh of fibrin fibers. Each of the clotting proteins has a very specific function, and the three main ones are prothrombin, thrombin, and fibrinogen. Thrombin promotes the conversion of fibrinogen into long insoluble fibers or threads of another protein – fibrin. Fibrin threads wind around the platelets forming an interlocking network of fibers and a framework for the clot. This net of fibers traps and helps hold platelets, blood cells, and other molecules tight to the material surface, forming a blood clot also referred to as a thrombus.

It has long been established, in the field of biomaterials, that bio- and hemocompatibility is mainly governed by the surface properties of the material that contacts the blood (Cooper 1982; Lelah and Cooper 1986; Schamberger and Gardella 1994). Predictions about the interactions between the biomaterial surface and the adsorbed proteins can only be formulated by having an exact knowledge of the structure of the biomaterial's surface and the conformation of the adsorbed proteins. These interactions are determined both by the hydrophobic/hydrophilic, charged/uncharged, and polar/nonpolar parts of the proteins and the properties of the polymer surface such as chemical composition,

morphology, charge, wettability, and topography (Dawids and Bantjes 1986; Williams and Williams 1989; Stamm 2008).

Hemocompatibility properties of surface materials can be evaluated following the ISO10993-4 (Biological evaluation of medical devices, Part 4: Selection of tests for interactions with blood. Geneva, Switzerland: International Organization for Standardization; 2002) guidelines in terms of protein adsorption, hemolysis, platelet adhesion and platelet activation, whole blood clotting time, and clinical coagulation times.

Hemocompatibility properties of surface materials can be evaluated in vitro according to the ISO 10993-4:2002 standard (ISO standard) guidelines in terms of hemolysis, thrombosis, platelet adhesion and activation, protein adsorption, and clinical coagulation times. The three categories of effects on blood most commonly evaluated are hemolysis, thrombosis, platelet adhesion, and activation (Imai and Nose 1972; Goodman et al. 1989; Allmér et al. 1990; Haycox and Ratner 1993; Tze-Man et al. 1993; Bahulekar et al. 1999; ASTM International 2000).

Damage to the membrane of red cells, as a result of blood exposure to foreign materials, can be evaluated by the hemolysis test. Hemolysis can be assessed by quantification of released hemoglobin (Hb) after contact between blood and sample, according to the ASTM F 756-00 standard. The Hb concentration can be determined by colorimetry at 540 nm, with a UV/VIS spectrophotometer. In the cyanmethemoglobin method (Moore et al. 1981; Van Assendelft et al. 1996; Zwart et al. 1996), blood samples with a plasma Hb concentration below 2 mg/mL are diluted in PBS in order to obtain blood with a total Hb concentration of 10 ± 1 mg/mL. The contact between diluted blood and membranes with an area of at least 7 cm² is maintained for at least 4 h of static incubation at 37 °C, and after which the blood is centrifuged, the supernatants are analyzed for their Hb content. Two controls are commonly used: distilled water (positive control) and PBS solution (negative control). The hemolysis degree is expressed through the hemolytic index (HI), calculated as follows:

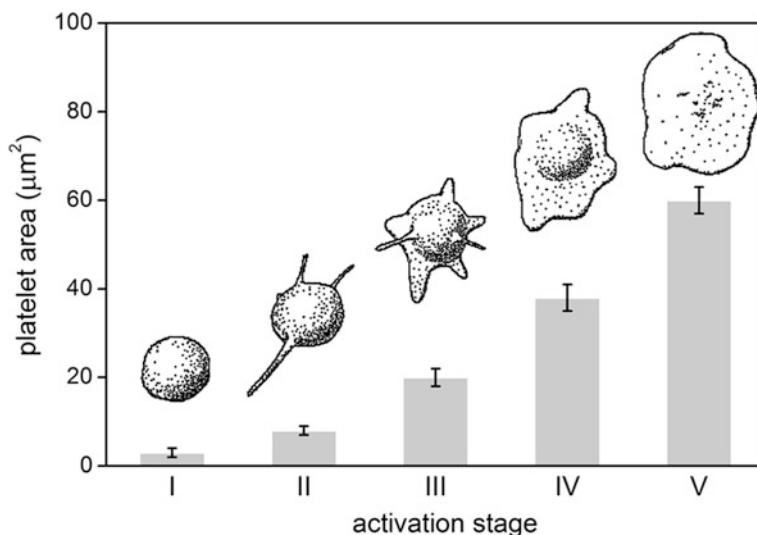
$$HI = \frac{[Hb]_{\text{released}} - [Hb]_{\text{negative control}}}{[Hb]_{\text{positive control}} - [Hb]_{\text{negative control}}} \times 100 \quad (1)$$

where $[Hb]_{\text{released}}$ is the concentration of Hb in the supernatant solution and $[Hb]_{\text{negative control}}$ and $[Hb]_{\text{positive control}}$ are the concentrations of Hb in the negative and positive controls, respectively. According to ASTM F-756, materials can be labeled nonhemolytic when the HI is between 0 and 2, slightly hemolytic when HI is between 2 and 5, and hemolytic when $HI > 5$.

Thrombosis can be evaluated through an assay based on the determination of the thrombus mass formed on the surface of the membranes after contact with static, recalcified blood, based on a modification of the gravimetric assay proposed by Imai and Nosé (1972) and Allmér et al. (1990). Samples of each membrane are cut into pieces with a surface area of 4 cm², and 250 μL of blood are carefully placed on top. The clotting process is then started by addition of 25 μL of 0.10 M CaCl₂ to the blood drop on the sample. The clotting process is stopped at different time periods by addition of distilled water. The thrombus formed at the surface of the membrane is fixed with formaldehyde and then washed with water. The thrombus mass is determined after drying the thrombus at 37 °C until a constant weight was reached. The results are expressed as a percentage of the thrombus mass formed on glass (positive control). A pre-weighted filter paper disk that followed the above procedure in parallel, but in the absence of a membrane sample and of blood, was used as a blank. From the thrombus mass formed on each sample, a thrombosis degree is calculated as a percentage of the thrombus mass formed on the positive control after subtracting the blank from each thrombus mass. A thrombosis degree of 100 % is assigned to the positive control;

$$\text{Thrombosis } \% = \frac{m_{\text{membrane}} - m_{\text{negative control}}}{m_{\text{positive control}} - m_{\text{negative control}}} \times 100$$

The interaction between platelets and the surface of the membranes can be evaluated by a technique often used by researchers based on the analysis of



Extracorporeal Blood Oxygenation Devices, Membranes for, Fig. 3 Diagram of the platelet spreading process divided into five shape categories for analysis and correlation between platelet categories and planimetrically determined platelet spread area. From *left to right*, the stages of spreading are defined as follows: stage I – round or discoid: no pseudopodia present; stage

II – dendritic or early pseudopodial: one or more pseudopodia with no evident flattening; stage III – spread dendritic or intermediate pseudopodial: one or more pseudopodia flattened, hyaloplasm not spread between pseudopodia; stage IV – spreading: hyaloplasm spread between pseudopodia; and stage V – fully spread: hyaloplasm extensively spread, no distinct pseudopodia

scanning electron microscopy (SEM) images (Goodman et al. 1989; Haycox and Ratner 1993; Tze-Man et al. 1993; Bahulekar et al. 1999). Platelet-rich plasma (PRP) is prepared by centrifugation of the pooled blood and is incubated with the membrane samples for 30 min at 37 °C. After incubation, the samples are fixed with glutaraldehyde post fixed with osmium tetroxide (OsO₄). After fixation the samples are dehydrated through a graded ethanol series to 100 % and dried by critical point drying. The dry samples are then observed by SEM. Quantitative and morphology analysis of platelets adhered to the surface of the membranes is carried out by imaging software.

In order to ensure the presence and activity of the platelets, glass is generally used as positive control for *in vitro* platelet response to foreign materials as it promotes enhanced adhesion and activation of platelets (Park et al. 1991; Amiji 1998).

The indicators of platelet adhesion used are platelet deposition (PD) and platelet coverage (PC), which are the number of adhered platelets/10,000 μm² of membrane surface area and the

percentage of the membrane surface area covered by platelets, respectively. The platelets are either passively attached and remain discoid and singular or may be activated subsequently. In the latter case, they progressively release their granule contents, thereby attracting further platelets, showing a typical shape change with flattening, formation of pseudopodia, and increasing area of contact. Scanning electron microscopic images of adhered platelets with magnifications of ×1,000 or ×2,000 magnification have been used by several authors for the quantitative analysis of platelet–material interaction. The extent of platelet spreading is examined by categorizing platelet shapes into five morphological forms describing increasing activation stages (I–V). These are discoid or round (stage I), dendritic or early pseudopodial (stage II), spread dendritic or intermediate pseudopodial (stage III), spreading or late pseudopodial (stage IV), and fully spread (stage V). The spreading stages and respective platelet areas are shown in Fig. 3 and defined in the legend (Allen et al. 1979; Goodman et al. 1984, 1989).

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Extraction Index

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The extraction index is a measure of membrane operation performance of extracting a desired species from the feed/retentate side in order to have it as permeate. It can be defined/evaluated for any involved species. It gives an indication about the real advantages offered by using a membrane unit instead of conventional ones. The higher the variable value, the higher the performance of the membrane unit. It is defined as the ratio (Eq. 1) of the permeate flow rate of the species permeated through the membrane to that totally fed to the membrane unit. Equation 1 shows different ways for evaluating the extraction index:

$$\begin{aligned}
 \text{Extraction Index}_i &= \frac{\text{Permeate flow rate}_i}{\text{Feed flow rate}_i} \\
 &= \frac{\text{Permeate flow rate}}{\text{Feed flow rate}} \frac{\text{Permeate molar fraction}_i}{\text{Feed molar fraction}_i} \\
 &= \frac{\text{Permeate flow rate}}{\text{Feed flow rate}} \frac{\text{Permeate Partial Pressure}_i}{\text{Feed Partial Pressure}_i} \\
 &= \frac{\text{Permeate flow rate}}{\text{Feed flow rate}} \frac{\text{Permeate concentration}_i}{\text{Feed concentration}_i} \\
 &= \frac{\text{Permeate flow rate}}{\text{Feed flow rate}} \frac{\text{Permeate mass fraction}_i}{\text{Feed mass fraction}_i}
 \end{aligned} \tag{1}$$

The extraction index assumes a specific and more interesting form when a chemical reaction takes place inside the membrane unit such as in the membrane reactors since a desired chemical can

be fed in it but also produced by reaction. In this case, Eq. 1 has to take into account also the production term:

$$\text{Extraction Index}_i = \frac{\text{Permeate flow rate}_i}{\text{Feed flow rate}_i + \text{Production by Reaction for } i - \text{th}} \quad (2)$$

If the water-gas shift reaction is used as an example, the extraction index can be defined as the ratio of the H_2 permeated through the membrane to that

totally available in the feed stream both as H_2 molecules and also obtainable from other chemicals (e.g., CO) by reaction, to the membrane unit (Eq. 3):

$$\begin{aligned} \text{H}_2 \text{ Extraction Index} &= \frac{\text{Flow rate}_{\text{H}_2}^{\text{Permeate}}}{\text{Flow rate}_{\text{H}_2}^{\text{Available in the feed}}} \\ \text{in the MR} &= \frac{\text{Flow rate}_{\text{H}_2}^{\text{Permeate}}}{\text{Flow rate}_{\text{H}_2}^{\text{Feed}} + a \cdot \text{Flow rate}_{\text{CO}}^{\text{Feed}}} \end{aligned} \quad (3)$$

$$a = \begin{cases} \text{H}_2\text{O/CO feed molar ratio} & \text{per } \text{H}_2\text{O/CO feed molar ratio} < 1 \\ 1 & \text{per } \text{H}_2\text{O/CO feed molar ratio} \geq 1 \end{cases}$$

The extraction index (Barbieri et al. 2008) takes into account the hydrogen fed as H_2 molecules and that is contained in the feed stream in other chemicals (e.g., H_2O). The term (a flow rate CO feed) of the Eq. 3 considers the maximum H_2 extractable from the chemicals (other than hydrogen) present in the system. The coefficient (a) takes into account the defecting reactant (CO or H_2O) by means of the feed molar ratio $\text{H}_2\text{O/CO}$. It (a) is equal to the feed molar ratio if the latter is lower than 1 (CO in defect with respect to H_2O). It (a) will be equal to 1 when the CO exceeds the H_2O . As defined, the extraction index is determined by the membrane properties, feed molar ratio, and CO conversion achieved in the membrane reactor, at set operating conditions.

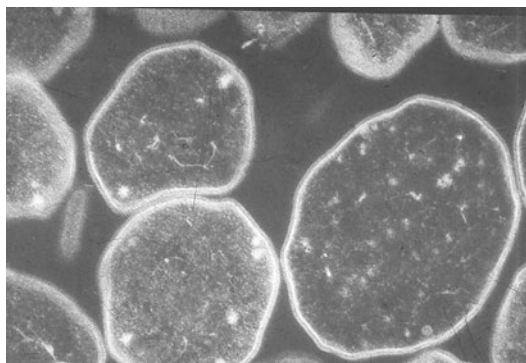
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Extremophiles

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The discovery of life in demanding environments continues to challenge conventional concepts of the growth-limiting conditions of many cellular organisms. Extremophiles may have diverse features; they may live at temperatures higher than 60 °C (thermophiles) or prefer colder sites, being able to grow between 5 °C and 20 °C; they may need pH <4 or >9 (acidophiles or alkaliphiles, respectively); or they can survive to high-salinity environments such as salty lakes (halophiles). They have been isolated in challenging biotopes from terrestrial solfataric fields to marine volcanic areas (Rothschild and Mancinelli 2001). The



Extremophiles, Fig. 1 Electron micrograph of *Sulfolobus solfataricus* MT4

phylogenetic assessment of the isolated species widens between Archaea, Bacteria, and Eukarya. There has been a steady increase in the isolation of these microorganisms documenting the enormous scientific effort in the last 30 years. Although major advances have been made in the last decade, our knowledge of the physiology, metabolism, enzymology, and genetics of this fascinating group of organisms is still limited. However there is little doubt that extremophiles will supply novel catalysts and will be a source of biomolecules with unique and biotechnologically relevant properties. It has been argued that membranes of extremophiles contain surfactants bearing unique stability that can be used in pharmaceutical and cosmeceutical formulations. Amylases, pullulanases, and glycosidases from hyperthermophiles were studied and proved efficient in starch biotransformation obtaining process throughput enhancement (Burg 2003). Trehalose-forming enzymes were found in *Sulfolobus shibatae* and *S. solfataricus* isolated in diverse solfatar fields worldwide (Fig. 1). Also lipases and esterases from thermophilic microorganisms and Archaea proved unique features (Schiraldi et al. 2002). Compatible solutes, of key importance for halophile survival, were isolated from *Halomonas* and *Marinococcus* species and thoroughly characterized proving their outstanding DNA/enzyme stabilization capacity; their commercialization was pursued by a

specifically founded company (bitop). Alkaliphilic enzymes were found as natural detergents, thus suggesting specific industrial interest. Psychrophilic enzymes may also be of applicative interest when biotransformations need to be carried out at low temperature. Other innovative products from extremophiles are cyclodextrins and polyunsaturated fatty acids, for which industrial applications are foreseen. Most of these kind of microorganisms isolated to date show specific needs to increase cell density. Recent alternatives to technological applications most commonly employed when the production of extremocompounds is approached at a bioreactor scale describe batch, fed batch, and continuous or in situ product removal fermentations in specifically developed bioprocesses. However, when large-scale production is needed for commercialization of these novel compounds, there is the need to bring together genetic and bioreaction engineering with separation techniques. The former prompted the development of specific plasmids and vectors to obtain a sound expression of extremophilic gene sequence and thus enzymes into mesophilic hosts; these recombinant strains are easier to cultivate, and the whole strategy is in fact recommended to solve the typical problems faced in extremophile-based bioprocesses and will serve to open up new opportunities for the development of unexplored fields such as renewable energies.

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Extremozymes

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The biocatalysts produced by extremophilic microorganisms, so-called extremozymes, are proteins with outstanding stability to temperature, pH, and organic solvents, thus becoming excellent candidates to improve industrial biotransformations (Schiraldi and De Rosa 2002). Polymer-degrading enzymes from hyperthermophiles, psychrophiles, and acidophiles may play an important role in food, detergent, and pulp and paper industry (e.g., amylases, pullulanases, xylanases, proteases). Extremozymes also include cellulases, proteases, pectinases, keratinases, lipases, esterases, catalases, peroxidases, and phytases. Owing to the unusual properties of these classes of enzymes, they are expected to fill the gap between biological and chemical industrial processes (Taylor et al. 2011). Despite this, actually few are the current processes based on these biocatalysts, the most known of which is the polymerase chain reaction (PCR) technology that in fact is based on DNA-modifying enzymes. Taq polymerase isolated from *Thermus aquaticus*. The use of this enzyme allowed the automation of PCR with a great advantage for research laboratories and industries. Beside this, few biocatalysts, used in diagnostics and starch liquefaction, are commercially produced by several biotechnology companies. Recently enzymes of interest in bioremediation have also been isolated from extremophiles: a thermoalkaliphilic catalase, which initiates the breakdown of hydrogen peroxide into oxygen and water, was isolated from *Thermus brockianus*, found in Yellowstone National Park, and operates over between 30 °C and 94 °C (pH range 6–10). Its outstanding

stability and wide operational range suggest application in hydrogen peroxide removal in pulp and paper bleaching, textile bleaching, food pasteurization, and surface decontamination of food packaging (Thompson et al. 2003). Enzymes isolated from psychrophiles, such as lipases, proteases, and cellulases, have been used as additives for the preparation of detergents working at low temperatures or in frozen food preparations. Furthermore, thermophilic enzymes have been used for the construction of optical nanosensors, stable and nonconsuming analytes. These innovative devices are based on the ability of thermophilic enzymes to bind the substrate at room temperature, without transforming it (de Champdoré et al. 2007). The binding of substrate to thermophilic enzyme is monitored as fluorescence variations of the enzyme. Many of these isolated enzymes have been cloned and expressed in mesophilic hosts to overcome the issues of extremophilic microorganisms cultivations, such as the unconventional fermentation parameters, special construction materials need, the low growth rates that are typical of most of these species, and the low biomass yield (despite the good enhancement proved in membrane bioreactors) (Schiraldi et al. 2001). The recombinant enzymes (Cimini et al. 2008), easily produced at high yield, may be commercialized, and furthermore, modern techniques like mutagenesis and gene shuffling will lead to in vitro tailored enzymes that are highly specific for countless industrial applications.

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Facilitated Pervaporation

Bart Van der Bruggen

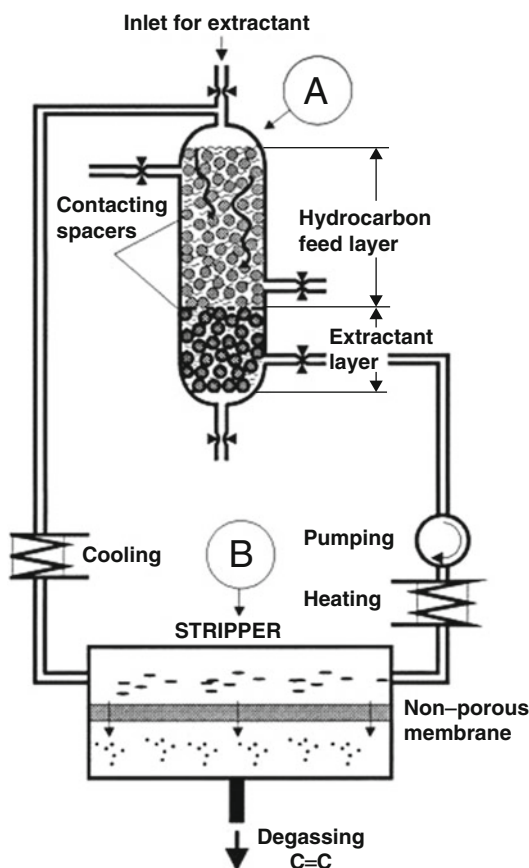
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A facilitated pervaporation system usually refers to the combination of a pervaporation as a separation unit combined with a chemical reactor for esterification reactions or other equilibrium reactions. The “facilitation” then refers in fact to the reaction, and not the separation. The pervaporation unit removes the side product of the reaction (in case of esterification, this is water) so that the reaction equilibrium shifts to a higher product yield (Van der Bruggen 2010). Other reactions than esterifications can also be facilitated, on condition that they concern an equilibrium reaction and that the side product can be easily removed by a pervaporation membrane (as is the case for water in an organic reaction mixture). For bioconversions, the reaction product(s) are to be removed instead of the by-products, in order to enhance the activity of the microbial population. This is the case, for example, in the production of bioethanol and in ABE (acetone, butanol, ethanol) fermentations, where ethanol (or butanol) is removed by a hydrophobic pervaporation membrane. See also pervaporation membrane reactor and

pervaporation assisted reactor for further explanation.

However, facilitated pervaporation may rather be related to a hybrid membrane extraction system, as described by Bessarabov et al. (1999) for the separation of liquid olefin/paraffin mixtures in the range up to C6. Nonporous polymeric membranes are used in a membrane contactor and a high-boiling-point selective liquid extractant flowing along polymeric membranes between the extractor and the membrane stripper. The olefin components permeated through the polymeric films at elevated temperatures in a membrane stripper, making it possible to obtain pervaporation transport. This is schematically shown in Fig. 1 (Bessarabov et al. 1999).

Another approach to obtain a pervaporation effect is by the use of fixed recognition sites in membrane contactors (Touil et al. 2006), so that the selectivity needed for pervaporation is obtained in a pertraction process (in which a porous membrane without any selectivity is used). The combination of selectivity characteristic for pervaporation and the pertraction effect results in an enhancement, which can be denoted as facilitated pervaporation. Cyclodextrins, for example, can be used to form inclusion complexes of different stability with organic molecules in the separation of p-xylene, m-xylene, and o-xylene (Touil et al. 2006). Kusumosahyo et al. (2004) made a similar study on polyacrylic acid (PAA) membranes and concluded that the native PAA



Facilitated Pervaporation, Fig. 1 Facilitated pervaporation using a hybrid membrane extraction system (for olefin separation). *A* is an extraction module, *B* is a membrane pervaporation cell (Reprinted with permission of Elsevier from Bessarabov et al. 1999)

membrane was almost impermeable for the xylene isomers, and the incorporation of cyclodextrins in the PAA membranes resulted in membranes having a molecular recognition function, which selectively facilitated the transport of the xylene isomers.

A further use of the term facilitated pervaporation refers to the membrane material itself. Liu et al. (2011) incorporated Ag(+) loaded titania (TiO₂) microspheres into a poly(dimethyl siloxane) (PDMS) matrix for pervaporative desulfurization of model gasoline and demonstrated facilitated transport through these membranes, as could be seen from increased fluxes and separation factors. A similar enhancement effect was

obtained by the incorporation of carbon nanotubes (CNTs) in the pores of a polyvinylidene fluoride (PVDF) membrane (Sae-Khow and Mitra 2009), and for polyvinyl alcohol (PVA) membranes (Bryant et al. 1997), and many other publications can be found on similar effects in mixed matrix membranes, nanoparticles-enhanced membranes, and hybrid organic–inorganic membranes. Chemical modifications have also been studied for enhancement of pervaporation. Wu et al. (2002) studied cross-linked polydimethylsiloxane (PDMS) membranes modified by the sequential introduction of two different side-arm functional groups, $-(CH_2)_3OC_2H_5$ and $-(CH_2)_3NMe_2$, for the pervaporative recovery of p-cresol from aqueous streams, which was successful.

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Facilitated Transport

Gerardo León

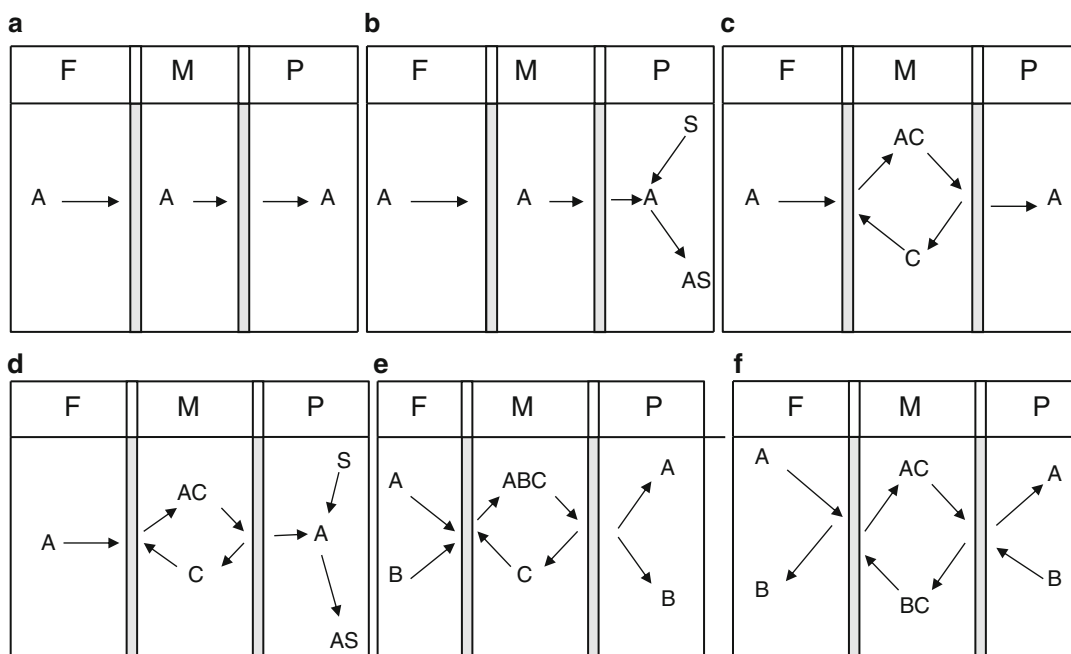
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Synonyms

Assisted transport

Transport mechanism used to improve flux, permeability, and selectivity in separations by liquid membranes. Mass transport selectivity and transfer velocity in a liquid membrane are mainly determined by the solubility and the diffusion coefficient in the membrane phase of the component to be separated. The driving force of the transport process is the gradient of chemical potential, normally due to a concentration gradient between the feed and the product phases. Then, a component which is soluble in the membrane phase and whose concentration is different

at both sides of that membrane phase will be transported through it (Fig. 1a). The component does not react chemically in the liquid membrane, and then it remains in the same chemical form in the feed, in the membrane, and in the product phases. Transport will end when an equality of concentration of the component prevails on both sides of the membrane phase. In order to improve the effectiveness of the separation process, facilitated transport mechanisms have been described (Vitt et al. 2010), which maximize both the extraction velocity (flux through the membrane phase) and the reception capacity of the diffusing specie in the product phase. Moreover, facilitated transport mechanisms combine the process of extraction and stripping in a single unit operation, and they offer the possibility of transporting a component against its own concentration gradient (Ho and Li 1992; Kislik 2010). Two types of facilitated transport are usually considered: type 1 and type 2. In type 1 facilitation, a stripping agent is added to the product phase, which quantitatively reacts with the diffusing specie to yield a membrane-insoluble product (Fig. 1b). Thus, concentration of that specie is reduced to zero in the



Facilitated Transport, Fig. 1 Schematic representation of the different transport mechanisms in liquid membranes

product phase, resulting in a high concentration gradient across the membrane phase. In type 2 facilitation (carrier-mediated transport), a reagent is incorporated in the membrane phase to carry the diffusing specie across the membrane to the product phase. The carrier forms, reversibly with the specie to be separated, a compound which is soluble in the membrane. This compound is formed in the interface feed phase/membrane phase, it is transported through the membrane phase due to its concentration gradient, and it is broken in the membrane phase/product phase interface. The specie to be separated is then liberated in the product phase, and the carrier diffuses in the contrary way through the membrane phase, as a consequence of its concentration gradient, to the opposite interface, to initiate a new separation cycle (Fig. 1c). As the process ends when the concentration of the specie to be separated equalizes on both sides of the membrane phase, carrier-mediated transport can be improved by incorporating a chemical reaction on the receiving side, as illustrated in Fig. 1d. The concentration of the specie to be separated is reduced to practically zero on the product side through an auxiliary reaction in the product phase, to form an insoluble compound in the membrane. The transportation of two components is possible, both from the feed phase (Fig. 1e) or one from the feed phase (the component to be separated) and the other from the product phase (Fig. 1f). Both cases are known as coupled transport, the first being denominated cotransport and the second counter-transport.

Cross-References

► Carrier-Mediated Transport

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Farmin 08

► Alamine 336

Fat Hydrolysis, Membrane Operations of

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Lipids that are solid at room temperature are termed fats. In nature, most fats are triglycerides – consisting of a glycerol backbone, to which three individual fatty acid moieties are attached. The variety of fats in nature and their diversity in terms of physicochemical properties come from the number of combinations of the hundreds of existing fatty acid residues – which, due to their underlying metabolic synthesis pathway, are characterized by an even number of carbon atoms.

In view of their insolubility and the relevance to water-based life, fats often appear stabilized via emulsification in aqueous media; this is notable in the case of milk fat, with globules surrounded by a membrane containing proteins and phospholipids. Said native globules range in size from less than 1 μm to over 10 μm . The uneven size distribution provides larger globules with a tendency to float: under static conditions, that buoyancy effect leads to creaming at the top of the container, but the process may be speeded up by centrifugation or filtration. The major disadvantage of the latter is the difficulty in removing the fat layer once

formed – coupled with clogging of the membrane pores – which is particularly detrimental in the case of hydrophobic matrices. Milk is often homogenized by forcing it into a tiny nozzle under high pressure, so as to reduce the average globule size to less than 1 μm ; this creates a more uniform distribution of globules that improves kinetic stability of the emulsion (Fox and McSweeney 1998).

Hydrolysis of fats can be effected by lipases (and esterases, to a lesser extent), which require a fat/water interface be present; this type of interfacial reaction is thus promoted by high specific areas, which may be attained at the expense of addition of emulsifiers and vigorous stirring. However, lipases are typically much more expensive than their fat substrates, so some form of immobilization thereof is in order for economic feasibility; this approach is particularly simple because such enzymes do not require cofactors for catalytic activity, while possessing a relatively high hydrophobic nature that facilitates spontaneous adhesion to hydrophobic materials via adsorption.

Several immobilized microbial lipases are available from industrial suppliers, using, e.g., ion exchange resins and polymeric materials as supports; they have been applied to hydrolyze fats in emulsified form, but show the disadvantage that the fat and enzyme particles must collide for catalysis to occur. Porous membranes constitute an interesting alternative, because lipase can be immobilized inside their pores – with water pumped along one side and (melted) fat along the other. Besides low rates of fouling, said tangential membranes may offer high volumetric efficiencies – especially if they are manufactured in hollow-fiber form – and permit the concentration of fat to remain at its maximum level ever by circumventing phase mixing.

Furthermore, immobilized lipase processes offer fatty acid- and stereo-specificity advantages over plain acid- or base-catalyzed hydrolysis of fats – which are intrinsically nonspecific. Considering the difference in metabolism of fatty acids depending on their original regiodistribution and chain length, lipases have been largely applied to produce tailor-made derivatives of triacylglycerols with medium- or short-chain fatty acid residues in external positions (*sn*-1 and *sn*-3) and long-chain fatty acids in the internal position (*sn*-2) (Willis

et al. 1998); these are in higher and higher demand for nutritional purposes.

Depending on the level of water in their vicinity, membrane-immobilized lipases operating on a fat substrate may also perform ester synthesis, as well as interesterification – of the acidolysis, alcoholysis, and transesterification types – depending on whether the aqueous substrate is replaced by a fatty acid, an alcohol, or another fat, respectively. This process is relatively easy to bring about, but suffers from two major shortcomings: enzymes tend to deactivate as time online elapses, thus calling for enzyme makeup; and product separation is often difficult, especially when only lipid phases are involved – and resorts to distillation (which should be carried out at low pressure in the case of heat-labile fats).

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Fat Processing, Membrane Operations of

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Fat processing is an active business, designed to create added value from slaughter by-products downstream the animal chain. It encompasses activities dealing with production of animal fats (and proteins) suitable for human consumption in agreement with directive 77/99/EEC (EU 1997),

as well as processing of category 3 (formerly labeled low risk) materials from animals approved for human consumption in agreement with regulation ABPR 1774/2002/EC (EU 2002). Fat processing has historically been associated with manufacture of high-grade animal fats for specific markets, e.g., bakery industry, calf milk replacers, and pet food – as well as commodities for formulation in the oleo-chemical industry (e.g., manufacture of soaps) and cosmetics; it uses bovine tallow, porcine lard, and poultry fat as major feedstocks.

The basic operations in fat processing are wet melting and dry rendering – or hybrid systems thereof. Fat tissues are subjected to relatively mild processing conditions to minimize their decay – but high-quality final products hinge critically on the quality and source of the raw materials. They are usually collected from slaughterhouses from animals slaughtered on the same day and undergo strict food safety steps according to HACCP methodology – including monitoring of environmental contaminants, growth hormones, and veterinary drugs. Membrane processing is possible, but only on clean melted fat – and chiefly to deliver support for enzymes aimed at controlled chemical modifications of such fat, e.g., interesterification.

Fat interesterification can be carried out via chemical or enzymatic processes; the former require metal alkalis as catalysts, but produce random interchange of acyl groups, lead to contamination of the final product with residual catalyst, and allow formation of soaps – all of which are viewed as drawbacks relative to their enzymatic counterparts (Erickson 1995). Lipase-mediated interesterification with lipases is characterized by great versatility, reasonable substrate selectivity (including regio- and enantioselectivity), possibility of operation at room temperature and pressure, and the absence of side reactions. To fully exploit the technical advantages of such enzymes, economic feasibility recommends the use in immobilized form – to extend their useful life, avoid product contamination and consequent instability, and circumvent the need for emulsification (James et al. 2009). Lipase immobilization also facilitates product separation,

enhances thermostability, alleviates rate dependence on pH, and is more flexible in terms of reactor configuration.

Unlike hydrolases at large that operate in plain aqueous phases, lipases are activated only in the presence of water/lipid interfaces – provided by the contacting surface between the immiscible aqueous and fat phases, which can be made to coincide with a porous membrane. Techniques that met with industrial success for immobilization of lipases include adsorption, covalent binding, and entrapment/microencapsulation (Knezevic et al. 2004). Note that the economic feasibility is directly related to the volumetric productivity on the long run, which depends in turn not only on the operational stability of the enzyme but also on its actual activity – which is normally lower than that of free enzyme, in addition to mass transfer constraints (Vulfson 1994).

Physical adsorption is the simplest method for lipase immobilization; binding occurs via hydrogen bonds, salt linkages, and van der Waals forces. The process is carried out at mild conditions, without (or with a marginal) support activation and in the absence of extraneous reagents; it is thus prone to preserving enzyme activity and specificity. The chemical nature of the carrier (including the ratio of hydrophilic to hydrophobic groups), the particle size and porosity, and the surface area available determine the amount of enzyme bound, as well as the enzyme behavior following immobilization (Cao 2005).

Chemical reaction between activated amino acid residues far from the catalytic and binding site of the enzyme and active functionalities on the carrier is the basis of (effective) covalent attachment. This is clearly the most efficient mode of immobilization – despite its being much more detrimental for enzyme activity, complex in terms of implementation, and heavily dependent on the properties of the carrier (Cao 2005).

Finally, entrapment involves capture of enzyme within a polymeric matrix during the polymerization process – whereas (the related) microencapsulation entails confinement by a membrane-like physical barrier around the enzyme preparation; entrapped enzymes may be further microencapsulated. Both processes require

simple equipment and relatively inexpensive reagents – and yield a better stability and an activity similar to adsorbed enzymes (Cao 2005).

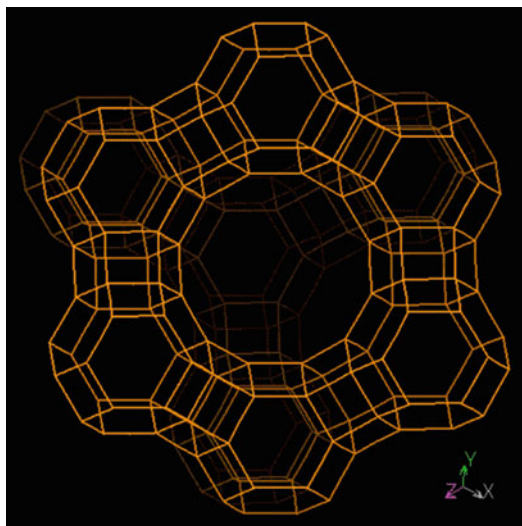
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Faujasite

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FAU (faujasite) belongs to the family of aluminosilicate molecular sieves defined by the formula $[(Ca, Mg, Na)_29(H_2O)_{240}[Al_{58}Si_{134}O_{384}] - FAU$ (www.iza-online.org). Two types of synthetic FAU zeolites referenced as Linde X and Linde Y differ in Si/Al atomic ratio, which is typically in the range from 1 to 1.5, one to two for the X and higher for the Y zeolite. The 24-tetrahedra cuboctahedral units (sodalite cages) in the FAU framework type are connected via hexagonal prisms (double six-rings) forming a three-dimensional porous channel structure along [110]. These are characterized by 12-oxygen ring



Faujasite, Fig. 1 The FAU-type zeolite supercage – view along [111] direction (International Zeolite Association (IZA))

window openings with the aperture of 8 Å and supercages of approximately 12 Å (McCusker and Baerlocher 2001). The FAU-type zeolite supercage viewed along [111] is shown in Fig. 1 (International Zeolite Association (IZA)).

The combination of large void volume and large pore openings in a three-dimensional channel system makes FAU thermally stable molecular sieve ideal for many catalytic, ion-exchange, and adsorption applications. FAU zeolites are generally synthesized by hydrothermal crystallization of reactive alkali metal aluminosilicate gels or clear solutions at low temperatures (70–300 °C, usually 100 °C) and pressure (autogenous) under alkaline conditions. Starting typically from sodium aluminate and sodium silicate, the zeolite is obtained in its Na^+ form (Blatter and Schumacher 1991). Replacement of the Na^+ cations by protons (leading to the H-zeolite form) is required for applications in acid catalysis. In addition, for specific catalytic applications, incorporation of various metal cations into the structure is carried out by impregnation or ion exchange and results in modification of the number and nature of acid sites influencing the diffusion of reactants and products. X-type zeolite has a wide range of industrial applications for gas or vapor adsorption, separation, and as catalyst (isomerization of

1-butene, alkylation of toluene with ethylene or methanol, cycloaddition of carbon dioxide to ethylene oxide (Ribeiro et al. 1984)). However, in many large-scale industrial applications, its chemical analogue with Si/Al ratio higher than 1.5 (zeolite Y) has superseded zeolite X because of its higher chemical and thermal stability. USY (ultra-stable Y zeolite prepared by dealumination of zeolite Y) is one of the most widely employed zeolitic materials in the petrochemical industry, essentially as a fluid cracking catalyst (FCC) of heavy petroleum distillates, for increasing the yield of gasoline and diesel fuel from crude oil. Considering membrane applications, the production of tubular FAU zeolite membranes has been mainly considered for alcohol dehydration by vapor permeation (Sato et al. 2008).

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Feed Pressure

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Membrane operations, for instance, membrane reactors, membrane gas separators, membrane contactors, membrane emulsifiers, membrane

crystallizers, reverse osmosis, nanofiltration, ultrafiltration, microfiltration, etc. as well the more conventional unit operations, like reactors, distillation columns, adsorbers, absorbers, liquid-liquid extractors, filters, pipelines, etc., are fed by a stream entering the unit. The pressure of this stream (to be treated by the unit operation) at the entering section of each unit operation is defined as feed pressure.

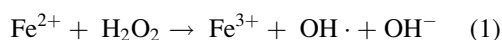
A further specification is required for membrane systems. Often, an auxiliary stream named “sweep” is fed to the membrane unit. This stream is characterized by a different pressure named “sweep pressure”; this pressure cannot be referred to as “feed pressure.”

Fenton Test

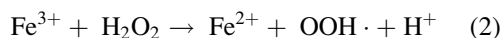
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Fenton’s reagent was developed in the 1890s by Henry John Horstman Fenton as an analytical reagent (Fenton and Jones 1900). It is a solution of hydrogen peroxide and an iron catalyst. Iron (II) sulfate is a typical iron compound in Fenton’s reagent.

The mechanism mostly accepted today, suggested by Haber and Weiss in the 1930s (Haber and Weiss 1932), is that iron(II) is oxidized by hydrogen peroxide to iron(III), a hydroxyl radical and a hydroxide anion (reaction 1):



Iron(III) is then reduced back to iron(II), a peroxide radical and a proton by the same hydrogen peroxide (dismutation reaction 2):



In the overall reaction, two molecules of hydrogen peroxide are converted into two radicals and water by the presence of catalytic iron ions.

The free radicals generated by Fenton's reagent induce then secondary reactions: the free hydroxyl radical is a powerful, non-selective oxidant used to oxidize organic contaminants in waste waters to primarily carbon dioxide and water.

Nowadays, Fenton's test is applied for the accelerated testing of the oxidation stability of proton exchange membranes (PEM) for fuel cell applications (Healy et al. 2005). Generally, the weight loss after a defined treatment time is used to monitor membrane degradation. Typical Fenton's test conditions for PEM membranes are an aqueous solution with 30 % H_2O_2 and 20 ppm Fe^{2+} at 80–90 °C with three treatment cycles with fresh reagent and 24 h per cycle. Given that the initial H_2O_2 concentration is much higher than in an operating fuel cell, "softer" alternative conditions are also used with an aqueous 3 % H_2O_2 solution mixed with 4 ppm Fe^{2+} at 68 °C (Ramaswamy et al. 2008).

Although Fenton's test is straightforward and considered as a benchmark for PEM evaluation, it has inherent limitations, given that the membrane degradation in this test is not related to an electrode process and does not involve variations in fuel cell operating conditions, e.g., operating potential, relative humidity, and the presence of fuel and oxygen.

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Fiber Models

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A fiber model is a model that uses straight or curved fibers, either finite in length or infinitely long, to represent the solid phase in a porous material or a reinforcement component in a composite material. Fiber models are the appropriate choice for modeling fibrous media, woven or non-woven, typically synthetic but occasionally also natural ones. Typical examples include the representation of membranes and porous media for fuel cells (Mathias et al. 2003), filters for the separation or sieving of particulate matter, or filters for the exclusion of bubbles in diverse applications of microfluidics. There is a recent rapid growth of interest in the utilization of fiber models for the description of the structure of gas diffusion layers in fuel cells but also of modern textiles and fabrics for specialized applications (Thiedmann et al. 2009; Gaiselmann et al. 2012). The typical features that characterize a fiber model include the diameter and length of the fiber, the number or length density per unit volume, the solid fraction, the shape of the fibers, and the elastic properties of the fibers that determine the macroscopic mechanical properties of the material. Carbon cloth, electrospun polyacrylonitrile, and polyester are common examples of fibrous materials that can be represented by fiber models. To convert to a pore model, various attempts have been made to infer some effective pore sizes from the fiber model, usually with the help of inscribed spheres among neighboring fiber segments. Skeletonization of a fiber model is often part of the analysis routine to facilitate the comprehension of the fiber cluster articulation and the eventual determination of the topology of the system. Useful concepts from straight-line path statistics or randomness of secant distribution through convex bodies (Coleman 1969) are incorporated in this type of models. The fibers can be hollow or

solid, randomly oriented or ordered to arbitrary degree, and either charged or neutral depending on the application. Fiber models of membrane materials and, more generally, fibrous media lend themselves to the numerical simulation of transport phenomena through their structure, usually diffusion, single or, two-phase flow, dispersion, particle attraction and deposition, combined phase transition and flow, heat conduction, electrical conduction, and light transmission (Torquato 2002; Tomadakis and Sotirchos 1993).

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FIB-SEM Tomography

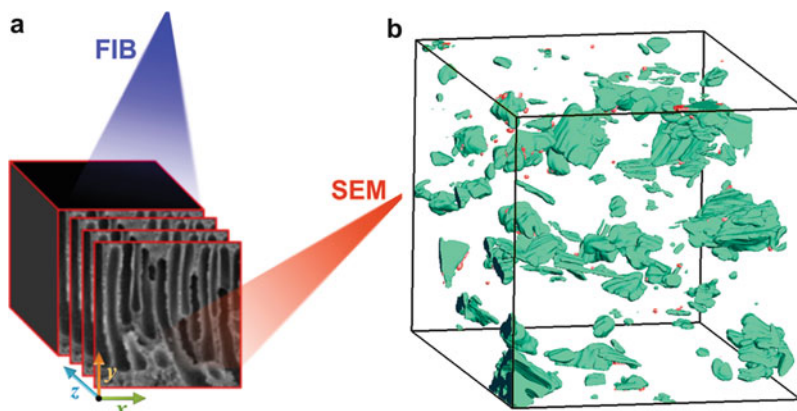
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FIB-SEM tomography (also known as tomographic FIB-SEM) is a micrometer-to-nanometer scale imaging technique which combines a focused ion beam (FIB) (Yao 2007) with a scanning electron microscope (SEM) (Goldstein et al. 2003) to obtain information on the internal structure of solid specimens. Focused ion beams

were developed in the early 1970s as a tool to either etch or deposit material on solids with (sub-) micrometer precision, via either volatilization or deposition processes, respectively, assisted by a beam of ions. They soon became an essential micromachining tool in the semiconductor industry. Later, the FIB technology was integrated into SEM devices. Such combination enables direct imaging of those solid surfaces previously processed with the FIB via detection of either backscattered or secondary electrons. A FIB-SEM device comprises a built-in FIB gun and a SEM detector, typically oriented forming an angle of 52–55°. Advances in FIB resolution and automation have paved the way to FIB-SEM tomography. *Tomography*, from Ancient Greek terms *tomos* (slice) and *grapho* (to write, to record), refers to the possibility of reconstructing the three-dimensional structure of an object, or a selected internal plane, by gathering information on discrete thin slices or two-dimensional projections of said object.

In a typical FIB-SEM tomography experiment, the specimen, often embedded in a resin, is situated at the coincident point of the FIB and SEM beams. Generally, solid specimens are previously sputtered with metal overlays to protect the sample surface during FIB milling and to increase its conductivity, in the case of specimens with insufficient electrical conductivity, thereby preventing charging effects in the course of the experiment. A trench is first carved on the upper surface of the sample with the FIB. Then several cross-sections of the internal structure of the specimen, exposed upon sequential erosion of thin layers with the FIB, are consecutively imaged with the SEM. Figure 1a depicts schematically the working principle of the serial milling and imaging procedure in FIB-SEM tomography.

The outcome is a stack of SEM micrographs of the consecutive cross-sections, which after alignment and further processing serves to reconstruct the investigated volume in three dimensions (tomogram). Typically, sample volumes in the range of 1–50 μm^3 are studied in a single FIB-SEM experiment. 3D imaging resolutions down to 10–30 nm can be achieved with modern equipments, being the limiting factor the resolution in the *z*-direction, i.e., the FIB-milling



FIB-SEM Tomography, Fig. 1 (a) Schematic representation of the alternating FIB-milling and SEM-imaging during a FIB-SEM tomography experiment on a membrane specimen. (b) 3D, surface-rendered view of a reconstructed FIB-SEM tomogram of a mixed-matrix

membrane incorporating metal-organic-framework (MOF) crystals within a polymer matrix. MOF particles are depicted in *green*, membrane void defects are shown in *red*, while the polymer matrix is depicted transparent (Rodenas n.d.)

direction. Such resolution closes the gap between other three-dimensional imaging methods such as electron tomography, which relies on transmitted electrons, and techniques based on X-rays such as X-ray tomography. As a result of the detailed and three-dimensional information provided on the internal structure of a wide array of solid specimens, FIB-SEM tomography has become an outstanding tool in a number of scientific and technological disciplines, including life-, earth-, and materials science.

Due to the typical sizes of membrane pores, ranging from nanometers to hundreds of micrometers, the resolution of this technique is suitable to study the internal porosity of a broad array of technologically relevant membranes, including analysis of different layer components in asymmetric membranes. In addition, the information gathered in FIB-SEM tomograms can be interpreted on a quantitative basis by combination with suitable image analysis methods (Haidekker 2011). In multicomponent membranes, FIB-SEM tomography enables assessing the proportion, degree of integration, and relative spatial location of different internal elements in three dimensions. As an example, Fig. 1b depicts a reconstructed FIB-SEM tomogram of a mixed-matrix membrane incorporating metal-organic-framework crystals within a polymer matrix. Three-dimensional visualization can also be applied to

image the most common membrane defects such as pinholes, cracks, or voids. In this respect, FIB milling represents an advanced solution to expose membrane cross-sections for imaging, as compared to more conventional approaches such as fracturing at cryogenic temperatures, which are prone to introduce a number of artifacts in the freshly generated surface to be imaged. The aforementioned structural features are known to be of significance for key performance parameters such as selectivity and permeability. Hence, detailed visualization of internal structures with FIB-SEM tomography contributes to the design and optimization of the membrane production and processing procedures. FIB erosion can also be applied to produce thin tips or slices from thicker membrane specimens, as required to be studied with complementary three-dimensional imaging methods such as atom-probe tomography, X-ray tomography, or electron tomography.

Cross-References

- ▶ [Asymmetric Membrane](#)
- ▶ [Membrane Micrograph](#)
- ▶ [Metal-Organic Framework](#)
- ▶ [Mixed Matrix Membranes \(MMMs\)](#)
- ▶ [Permeability](#)
- ▶ [3D-Imaging Methods for Membranes](#)

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Fick's Laws

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Fick's laws (first and second Fick's laws). These two laws of diffusion were originally postulated by the medical doctor Adolf Eugen Fick (1829–1901) (from whom they take their name) by analogy with energy transfer in conduction and not by experiment (Fick 1855; Bird et al. 2002).

First Fick's law. For a generic species A in a mixture, first Fick's law is referred to as the constitutive equation for mass flux of A stating the proportionality between flux and mass gradient in a certain domain, which can be used in solid, liquid, and gas phase (Bird et al. 2002; Krishna and Taylor 1993). This relationship can be expressed both in term of mass (Eq. 1) and molar quantities (Eq. 2) as

$$\underline{j}_A = -\rho D_A \nabla w_A \quad (1)$$

$$\underline{J}_A = -c D_A \nabla x_A \quad (2)$$

where j_A and J_A are the mass and molar flux of the species A, respectively; ρ [kg m⁻³] is the density of mixture; c [mol m⁻³] is its total concentration; w_A [kg_A kg⁻¹] and x_A [mol_A mol⁻¹] are the mass

and molar fraction of the species A, respectively; and D_A [m² s⁻¹] is the *multicomponent* diffusion coefficient, which generally depends on temperature, pressure, and species compositions. Equations 1 and 2 are vectorial equations, as flux is a vector. The scalar versions of Eqs. 1 and 2 along a specific direction (x) are provided by Eqs. 3 and 4, respectively:

$$j_A|_x = -\rho D_A \frac{\partial w_A}{\partial x} \quad (3)$$

$$J_A|_x = -c D_A \frac{\partial x_A}{\partial x} \quad (4)$$

For anisotropic media, the diffusion coefficient depends on the diffusion direction, and thus, it is a second-order tensor (Eq. 5) rather than a scalar:

$$\underline{\underline{D}}_A = \begin{bmatrix} D_{A,xx} & D_{A,xy} & D_{A,xz} \\ D_{A,yx} & D_{A,yy} & D_{A,yz} \\ D_{A,zx} & D_{A,zy} & D_{A,zz} \end{bmatrix} \quad (5)$$

In Eq. 5, the diffusivity matrix is expressed with respect to a general reference system. In general, the multicomponent diffusion coefficient is not directly known, it being obtained, on the contrary, from the *binary* diffusion coefficients, which can be measured experimentally and for which semiempirical relationships are available in the literature. The relationship between the multicomponent diffusion coefficient and binary diffusion coefficient is extensively reported, for example, in the book of Krishna and Taylor (1993).

Second Fick's law. For a generic species A in the mixture, the mass conservation law (scalar) within a tiny control volume can be expressed both in terms of mass quantities (Eqs. 6, 7, and 8),

$$\frac{\partial(\rho_A)}{\partial t} = -(\nabla \cdot \underline{n}_A) - (\nabla \cdot \underline{j}_A) + r_A \quad (6)$$

$$\underline{n}_A = \rho_A \underline{v} \quad \rho_A = \rho w_A \quad (7)$$

$$\underline{v} = \sum_{i=1}^n w_i \underline{v}_i \quad (8)$$

and molar quantities (Eqs. 9, 10, and 11), analogously to what is reported for *first Fick's law*.

$$\frac{\partial c_A}{\partial t} = -(\nabla \cdot \underline{N}_A) - (\nabla \cdot \underline{J}_A) + R_A \quad (9)$$

$$\underline{N}_A = c_A \underline{v}^* \quad c_A = c x_A \quad (10)$$

$$\underline{v}^* = \sum_{i=1}^n x_i \underline{v}_i \quad (11)$$

where n_A and N_A are the mass and molar convective flux, r_A and R_A are the mass and molar generation terms – which can be positive (source) and negative (sink) –, and $\underline{v}_i$ is the arithmetic average of the velocities of all the molecules of the i th species in mixture within the control volume.

If there is no either net convective transport or sinks/source of mass within the control volume, Eqs. 6 and 9 are simplified to give Eqs. 12 and 13, which represent the common form of *second Fick's law*:

$$\frac{\partial(\rho_A)}{\partial t} = -(\nabla \cdot \underline{j}_A) \quad (12)$$

$$\frac{\partial(c_A)}{\partial t} = -(\nabla \cdot \underline{J}_A) \quad (13)$$

In *membrane technology*, *first Fick's law* is coupled with the second one to calculate flux and concentration profiles of the species along and through the membrane in reaction and separation processes. These are of practical interest to model the membrane behavior, to eventually optimize the operating conditions, and to maximize the process performance.

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Filler in Membranes

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Synonyms

Inorganic fillers

Composite perfluorosulfonic acid membranes containing different types of inorganic fillers such as hygroscopic oxides, surface-modified oxides, zeolites, inorganic proton conductors, etc. have shown an increased conductivity with respect to the bare perfluorosulfonic membranes at high temperature (Aricò et al. 1998, 2003). The presence of hygroscopic inorganic oxides inside the composite membrane besides extending the operation of perfluorosulfonic membranes (e.g., Nafion®) in the high-temperature range reduces the crossover effects by increasing the “tortuosity factor” in the permeation path. Such effects are particularly serious at high temperature in DMFC systems. An appropriate tailoring of the surface chemistry in these nanoparticles is a key step to enhance water retention at high temperature. Composite recast Nafion® membranes containing inorganic fillers have been employed in high-temperature (~150 °C) direct alcohol (Aricò et al. 1998) and H₂-air fuel cells (Watanabe et al. 1996). These composite membranes were originally developed for reduced humidification operation in polymer electrolyte fuel cells (Watanabe et al. 1996) due to the enhanced water retention inside the membrane by the effect of the inorganic filler (Aricò et al. 1998). A further advantage of composite membranes relies in the barrier effect given by the inorganic filler for methanol crossover (Ren et al. 1996).

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Finger-Like Structure

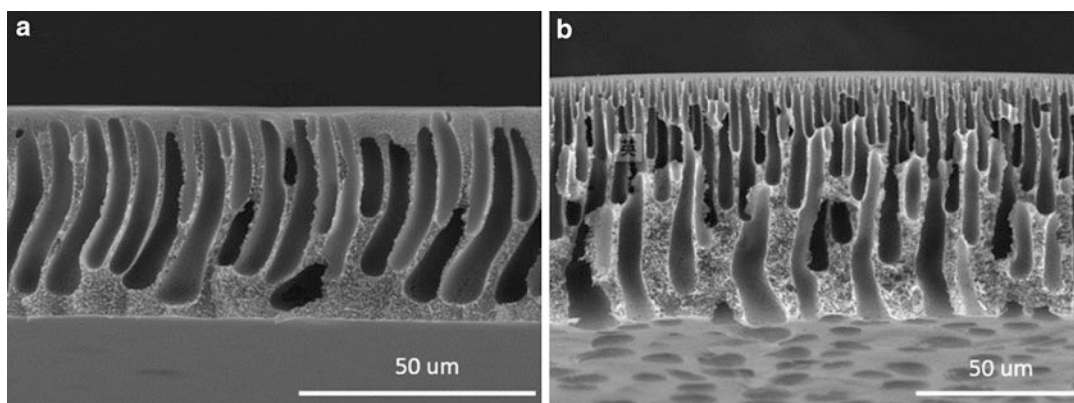
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Finger-like structure is one of the typical membrane structures, as shown in Fig. 1. It is also called macrovoid structure. Figure 1 shows asymmetric membranes with a thin top skin layer supported by a finger-like sublayer. Formation of finger-like structure follows two processes: pore initiation and growth. As a polymer solution undergoes a liquid-liquid phase separation, both polymer-rich and polymer-lean phases are

developed. The nuclei of the polymer-lean phases initiate the finger-like structure. The nuclei are mostly formed just beneath the top layer, and growth of the nuclei depends on the state of the solution in the frontier of the phase separation (Marcel 1996). The nuclei may grow if the polymer solution in the front is stable and could supply enough solvent (or solvent/nonsolvent) to sustain the growth. The growth ends when new nuclei are initiated in the frontier of phase separation or the concentration of the polymer-lean phases enters the glass transition point. At an extreme condition, the finger-like structure in the PSf membrane penetrates through the whole cross section because bottom PEI solution provides solvent to sustain the growth of the polymer-lean phases in the PSf layer (Xiao et al. 2015).

Finger-like structure is not strong enough for many applications due to the weak mechanical property, e.g., gas separation, nanofiltration, and reverse osmosis. Suppress of the finger-like structure is quite a scientific and artistic task for membrane scientists and engineers. Upon formation of nuclei of polymer-lean phases, if there is no solvent to sustain the growth, no finger-like structure would result. By adding a significant amount of nonsolvent into the polymer solution, it may generate simultaneously a lot of polymer-lean phase nuclei, thus preventing the polymer-lean phases from growing to full-sized finger-like macrovoid.



Finger-Like Structure, Fig. 1 Finger-like structure of a polyethersulfone flat sheet membrane. (a) Cross section of a PES ultrafiltration membrane; (b) cross section of a PSf membrane prepared by casting a PES/NMP

solution (17/83 wt.%) onto a PEI/NMP (20/80 wt.%) solution and then immersed in water for precipitation. The fingers penetrate through the membrane

Increasing the polymer viscosity may reduce the growth rate of the nuclei and allow more time for the formation of more nuclei in the front, leading to less finger-like macrovoids.

As a rule of the thumb, instantaneous demixing is generally related to the formation of a finger-like macrovoid structure. Therefore, by adding a solvent into the coagulation bath, choosing a solvent/nonsolvent (as the coagulant) system with low affinity is common practice to suppress the finger-like structure. For a certain solvent/nonsolvent pair, the hydrophobicity of the polymer is also crucial. For polar solvent/nonsolvent systems, e.g., NMP/H₂O, DMAc/H₂O, and DMF/H₂O, a PVDF/solvent solution will end up with a sponge-like structure due to the strong hydrophobicity of the polymer in nonsolvent-induced phase separation using water as the coagulant. However, by adding hydrophilic polymer additive into the PVDF solution, finger-like macrovoids are generated. Encouraging delayed demixing is key to prevent the finger-like structure, because onset of the nuclei is delayed and the top skin layer is densified. However, this is often unfavorable for membrane performance.

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Fixed Bed Catalytic Reactor

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The fixed bed (or packed bed) membrane reactor configuration is the first and most studied configuration for membrane reactors. This is because the

first studies on membrane reactors focused on the effect of the gas permeation through membranes on the reaction system (which is often a conventional packed bed reactor).

In a packed bed membrane reactor, the catalyst is confined in fixed bed configuration, and it is in contact with a permselective membrane. The most used packed bed configuration is the tubular one where the catalyst may be packed either in the membrane tube or in the shell side, while the permeation stream is collected in the other side of the membrane (in the case of hydrogen-selective membranes) or one reactant is feed on the other side of the membrane (in the case of oxygen-selective membrane).

For multitubular membrane reactor configurations, the catalyst in tube configuration can be preferred especially for construction reason and for the extent of bed-to-wall mass and heat transfer limitations which can be very detrimental in the catalyst in shell configuration.

Often, a sweep gas can be used in the permeation side of the membrane in order to keep the permeation hydrogen partial pressure as low as possible for minimizing the membrane area required for the hydrogen separation. This practice is, for example, very useful if hydrogen for ammonia plant is being produced, in which case an amount of nitrogen can be used for sweeping the permeation side producing a synthesis stream ($N_2/H_2 = 1/3$) ready for the final reaction step. If a sweep gas is used in the permeation side, then a packed bed membrane reactor can be used in both cocurrent or countercurrent modes.

An interesting feature of packed bed membrane reactors is the possibility to operate them in a reverse flow mode, integrating the reaction and separation with the recuperative heat exchange inside the reactor. This operational mode is quite interesting for partial oxidation of methane (POM) (Smit et al. 2005). In normal POM systems air and CH₄ feed streams have to be preheated to the reaction temperature, while being POM reaction only slightly exothermic, the external heat transfer between feed and exhaust is very expensive. Therefore, recuperative heat exchange is preferably carried out inside the reactor.

Although the tube in tube configuration is quite useful to work in lab scale and for proof of principle of membrane reactors, for industrial scale some other configurations need to be used in order to increase the membrane area per volume of vessel used. In fact, the amount of hydrogen produced is directly related to the amount of membrane area installed in the reactor. Starting for the tube in tube configuration, a straightforward way to increase the membrane area in packed bed is the tube in shell configuration (Buxbaum 2002; Tosti et al. 2008).

Although the packed bed configuration is very advantageous and easy to operate, the production of thin membranes brought under the spotlight one of the disadvantages of fixed bed membrane reactors: the influence of bed-to-wall mass transfer limitations on the membrane area required. Briefly, as long as the hydrogen flux through the membrane is a limiting step, the effect of external mass transfer limitations such as the limitations to hydrogen transport between the bulk of the catalytic bed (where hydrogen is produced) and the membrane wall (where hydrogen is recovered) can be neglected. However, by increasing the membrane flux, the external mass transfer limitations became limiting and determine the extent of membrane area. This has been demonstrated both experimentally (Peters et al. 2008) and numerically (Gallucci et al. 2010). This important drawback has driven the research toward new reactor concepts such as micro-membrane reactors or fluidized bed membrane reactors.

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Fixed Carrier Membrane

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Fixed (site) carrier membranes (FSC) combine the durability of a dense membrane with the selectivity of a supported liquid membrane (SLM) overcoming the limitation of SLM, degradation due to the wash out of the carrier solution over time. The carrier is either covalently bonded to the polymer chain (chained carrier) or immobilized in the polymer matrix by physical constraints or weaker ionic bonding. A fixed carrier membrane will separate mainly via facilitated transport mechanism, implying that the carrier will react specifically with one of the components to be separated.

Noble (1990, 1991) and Cussler (Cussler et al. 1989) developed two different models to describe the transport across fixed carrier membranes. E. L. Cussler explained the transport by “chained carrier” theory, when carriers are covalently bonded, requiring a certain mobility of polymeric chains and that a percolation threshold appears when two chained carriers are too far apart.

R. Noble described the transport of neutral molecules such as O₂ (Noble 1990) or ions (Noble 1991) across membranes in the terms dual-mode sorption model, assuming the presence of two distinct regions exhibiting gas solubility based on Henry’s law and Langmuir sorption isotherm. The model assumes also that permeation is diffusion-limited. This model shows the same behavior as facilitated transport in liquid membranes and does not predict a percolation threshold as “chained carrier” model does. The model implies that the

effective diffusion coefficient of the solute to be transported depends on the morphology of membrane between two reactive sites (“terrain”). Changes in polymer morphology cause a change in this effective diffusion coefficient.

The model presented by R. Noble is based on the model presented by Barrer (1984) assuming that a hole (microvoid) of the polymer free volume is equivalent to a complexing site (a carrier). Barrer’s dual-mode transport for glassy polymers contains four diffusion coefficients: diffusion of a compound (A) through the polymer matrix, diffusion of (A) from the polymer matrix to a hole in the Langmuir region (excess of free volume), diffusion of (A) between two holes, and diffusion of (A) from a hole to the polymer matrix. The significance of this analysis is that it predicts facilitated transport even when there is no diffusion or mobility of the complexing agent.

Both Noble’s and Cussler’s models have their limitations. Dual sorption model presented by Noble assumes that the concentration of the carrier is in large excess and consequently constant. This implies that the model will start to deviate from experimental results at high loadings of the carrier with the permeant (A) (carrier saturation). Also the model does not take into account the reaction kinetic between the carrier and permeant (A).

The hopping mechanism proposed by Cussler will strongly depend on the system permeant-membrane material characteristics even though it is taking into account the chemical reaction between the carrier and component (A): high diffusion coefficients of a compound (A) will allow facilitation effect even at low concentration of the carrier infirming a strict percolation threshold predicted by the model.

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Fixed-Site (Chained-Carrier) Membranes

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Carrier-facilitated transport processes in liquid membranes often achieve spectacular separations between closely related species because of carrier selectivity. The instability of supported liquid membranes (SLM) or emulsion type of membranes (ELM) is a major technical challenge for their implementation at large industrial scale (Mulder 2003; Baker 2004; Koros and Mahajan 2000). One approach to stabilize the membranes is to covalently link the carrier complex to the matrix polymer resulting in fixed-site carrier (chained) membranes.

The term *chained carrier* refers to transport mechanism theory rather than to position of the carrier on the membrane. E. L. Cussler (Cussler et al. 1989) explained the *facilitated transport* by a “chained carrier” theory that implies a certain mobility of polymeric chains and that a percolation threshold appears when two chained carriers are too far apart. Chained carriers, by comparison to mobile carriers diffusing freely within a liquid membrane, have limited diffusion because they are covalently bound in the polymer membrane. The solute is transported via a hopping (“Tarzan”) mechanism from one carrier to the next one between the two interfaces, feed and permeate sides of the membrane.

In order to transport components via facilitated transport, the polymeric chains must have a certain mobility degree, and the concentration of the carrier must be higher than the percolation threshold (Cussler et al. 1989).

The hopping mechanism proposed by Cussler will strongly depend on the system permeant-membrane material characteristics even though it is taking into account the chemical reaction between the carrier and a component (A): high diffusion coefficients of a compound (A) will allow facilitation effect even at low concentration of the carrier infirming a strict percolation threshold predicted by the model.

A particular case of “chained carrier” for CO₂ transport is presented by KT.J. Kim et al. (2013). The carrier is represented by the amine groups covalently bonded to the polymeric chain of polyvinylamine.

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Flat Sheet Membrane Module

► Cross-Flow Membrane Module

Flat Sheet Membrane Photocatalytic Reactor

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When membrane configuration is flat type and it is coupled to a photocatalytic reaction, the reactor can be named flat-sheet membrane photocatalytic reactor.

A recirculation cell containing various types of flat-sheet membranes which were able to retain the suspended catalyst and partially selective to the pollutant was studied by Molinari et al. (2001). The membranes were NTR7410 and NTR7450 (Nitto Denko), N30F and NF-PES-010 (Hoechst), and MPCB0000R98 (SEPAREM). The measured permeate flux was in the range 5–30 l/h m² at 4 bar, and all membranes showed both a rejection and a capacity to adsorb the pollutant with a transitory phase varying from 80 to 400 min at 4 bar. This behavior could be a benefit for the process because oscillations in the pollutant concentration were not transmitted in the permeate. Three factors, rejection, photocatalytic degradation, and adsorption, were able to maintain the 4-nitrophenol (4NP) concentration in the permeate at very low values. For the continuous system, the lowest 4NP concentration in the permeate was 6–7 % (w/w) of the initial 4NP concentration (40 mg/l) after a transient period of 300 min.

In another method, the catalyst, TiO₂ P25 Degussa, was immobilized by physical deposition on a flat-sheet polymeric membrane, and 4NP was used as a model molecule to evaluate the reactor performance (Molinari et al. 2000). A preliminary investigation of the stability, under UV irradiation, of some eligible polymeric membranes was carried out by using scanning electron microscopy (SEM), optical microscopy (OM), determinations of water permeation flux (WPF), and total organic carbon (TOC). These tests showed that commercial membranes made of fluoride + PP (FS 50 PP-Dow), polysulfone + PP (GR 51 PP-TechSep), and polyacrylonitrile (PAN-TechSep) seemed to be quite stable to UV light over a 24 h period of irradiation. Immobilization of TiO₂ onto membranes by ultrafiltrating TiO₂ suspensions showed an optimal layer density slightly >2.04 mg TiO₂ per cm² of membrane surface area. Results obtained from membrane reactor studies indicated that the observed initial rate constants for the degradation of 4NP were almost independent on the amount of TiO₂ employed over the range 0.76–4.08 mg/cm². A 50 % weight degradation of 4NP after 5 h of irradiation in the presence of air was obtained. An

almost complete degradation of 4NP, instead, was observed in the presence of TiO_2 suspended in the solution and pure oxygen. The permeate deriving from the membrane photoreactor was clear, and 4NP concentration was approximately equal to that found in the retentate. The possibility of the continuous reuse of the photocatalyst and the continuous separation of products from the reaction medium gave some advantages over traditional approaches.

A flat-sheet membrane photocatalytic reactor operates, generally, with suspended solids (the catalyst) and air bubbling (oxygen feed), so, in the following, some cases of interest for operating such reactors are reported.

Selection of a membrane configuration is a crucial step in the design process and has a high impact on further plant operations. Despite increasing experience with full-scale applications, practical knowledge concerning the impact of different membrane configurations on process performance and operational costs is still lacking. Full-scale performance data of a membrane bioreactor (MBR) comparing the use of flat-sheet and hollow-fiber membranes and analyses of the consequences on operation, performance, and treatment efficiency have been reported by Krzeminski et al. (2012). Hollow-fiber configurations, compared to the flat sheet, are designed for higher fluxes, operated at lower concentrations, cleaned more often, and protected by stricter pretreatment. Filterability of activated sludge from municipal MBRs was better than from industrial MBRs and did not depend on membrane configuration. The energy consumption depends more on the influent type than on the membrane configuration.

An aerated flat-sheet module focusing on the effect of bubble distribution on the spatial variation of surface mass transfer with intermittent slug bubbling was studied by Field et al. (2011). This mode of operation will delay the onset of the transmembrane pressure jump if biomass removal is more dependent upon maximum shear stress than mean shear stress. Two basic setups were considered: an orifice in the middle of the aeration tube, at the base, and two symmetrically placed orifices in the aeration tube. With relatively low

air rates, a single orifice generates a higher average enhancement than two orifices, but the reverse was found at a relatively higher air rate. The enhancement in the center area of the module was relatively higher than that of the edge regions when using a single orifice, but more uniformity was achieved with two.

Exploration of two major commercialized flat-sheet and hollow-fiber membranes in a submerged membrane fungi reactor fed with a synthetic textile wastewater revealed striking differences in the extent and mechanism of fouling between the two types, indicating a case-specific scope of choice between them for industrial wastewater treatment (Hai et al. 2005). The hollow-fiber membrane exhibited fouling with a cake layer composed of fungi and starch, intensity being proportional to the operating flux (0.05–0.3 m/d). Conversely, the flat-sheet membrane suffered from immediate internal pore blocking beyond a critical flux of $0.2 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$. During the experiment with major constituents of the synthetic wastewater separately, while media containing only starch and only dye induced negligible fouling, flux-dependent pore blocking was evident for both the hollow-fiber ($0.288 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$) and flat-sheet membranes ($1.3 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$) for the mixture of starch and dye. Despite that a remarkable 99 % color and 97 % TOC removal were achieved by both membranes, fouling with different modes and intensity for the two types under similar conditions and for the same type of membrane under different exposure conditions warrants development of suitable modules for such recalcitrant wastewater.

The oxygen transfer across a microporous, flat-sheet membrane with and without a nitrifying membrane-aerated biofilm (MAB) was studied by Shanahan and Semmens (2006). Clean membrane oxygen transfer was quantified via average mass transfer coefficients and local fluxes calculated from profiles of dissolved oxygen (DO) along the membrane length. Stoichiometric calculations and DO profiles were used to characterize oxygen transfer with a nitrifying MAB. Comparison of the local fluxes with clean and biofilm-coated membranes revealed that oxygen transfer was decreased in upstream sections of the membrane during cultivation of an

MAB due to reduced advection and/or turbulence near the membrane surface. By contrast, oxygen transfer was increased in downstream sections of the membrane via bacterial respiration. Oxygen fluxes generally decreased in the downstream direction with biofilm-coated membranes; however, variability in biofilm structure and membrane coverage altered this trend on several occasions. Furthermore, biofilm structures were observed to form via sloughing and settling of biomass at the membrane surface. Thus membrane configuration may have a significant influence on oxygen transfer rates in membrane reactors.

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Flavanoids Separation

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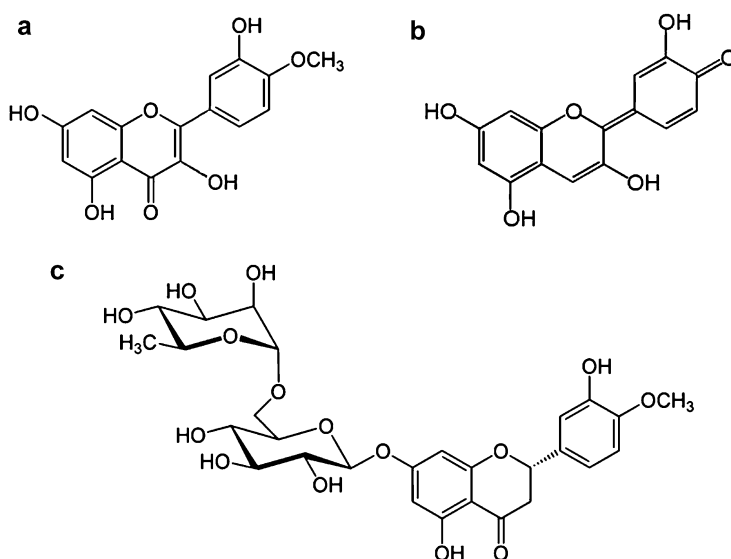
Flavonoids are a water-soluble class of polyphenols derived from plant secondary metabolites through the condensation of cinnamic acid with

malonyl-CoA groups (Bloor 2001). This conversion can lead to the formation of flavones, isoflavones, flavonols, and anthocyanins. Flavanoid chemical structures are based on a C6-C3-C6 skeleton that differs among each other by the saturation of heteroatomic ring C (Stobiecki and Kachilicki 2006). Further reactions as glycosilation, acylation, and alkylation cause the formation of a huge variety of flavonoids in the plant kingdom. The flavonoids consist of six major subgroups: chalcone, flavone, flavonol, flavanone, anthocyanins, and isoflavonoids. Examples of some of these subgroups are shown in Fig. 1. Together with carotenes, flavanoids are also responsible for the coloring of fruits, vegetables, and herbs. For analysis purposes, there is basically a flavonoids division into glycosides, aglycones, and anthocyanins. Each of these types is quantified by different analytical methods. The most important dietary sources are fruits, tea, and soybean. Green and black tea contains about 25 % flavonoids. Other important sources of flavonoids are apple (quercetin) and citrus fruits (rutin and hesperidin). Flavonoids are becoming very popular because they have many health-promoting effects. Some of the activities attributed to flavonoids include antiallergic, anticancer, antioxidant, anti-inflammatory, and antiviral activities.

Essential to the study of flavonoids is having the means available for their separation (analytical and preparative) and isolation. Thin-layer chromatography is a rapid, simple, and versatile method for fractionation flavonoids. However, this method has been substituted to qualitative and quantitative applications of high-performance liquid chromatography (HPLC). In HPLC analysis, flavonoids can be separated, quantified, and identified in only one operation by coupling HPLC to ultraviolet (UV), mass, or nuclear magnetic resonance (NMR) detectors. Another technique that has been gaining attention is capillary electrophoresis (CE). All the methods use the effects of the presence of the flavonoid phenyl ring which is an excellent chromophore and is responsible for the easy detection of flavonoids. Their UV spectra provide enough

Flavonoids Separation,

Fig. 1 Examples of some flavonoids. (a) quercetin – flavonol, (b) cyanidin – anthocyanin, (c) hesperidin – flavanone



information to distinguish the type of phenol (Marston and Hostettmann 2006).

Flavonoids can be also separated from each other by the use of a polymeric membrane. A relatively high concentration of polyphenolics and flavonoids present in the juices were fractionated by various methods including ultrafiltration to get a retentate that showed very high oxygen radical absorbance capacity (ORAC) even at 50 % recovery of thin juice (Kumar 2006). Membrane-based processes are usually more energy efficient than distillation, adsorption, and chromatography. Furthermore, membranes have the advantage of compatibility with a wide range of solvents and chemical products, ability to process thermally sensitive compounds, easy amenability to automation, smaller footprint, and seamless scale-up. These advantages open up several possibilities of membrane application in the production of bioactive compounds through preconcentration of dilute solutions, fractionation of a complex mixture, recovery of intermediates, and recycling of solvents. However, it is also important to be aware of the membrane-based separation drawbacks, such as limited selectivity, fouling leading to performance decline, cleaning, and higher capital costs in certain installations.

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Flexibility in Gas Separation

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The flexibility (also called easy of expansion) is the ability to operate under variable feed quality conditions, either on a short-term or long-term basis (Miller and Stöcker 1989; Brunetti

et al. 2010). The changes in feed composition occur very often in refinery applications, particularly when the source of the feed is a catalytic process or when the feedstock to the upstream unit changes as well as in flue gas streams.

In membrane processes, the increase in feed impurity concentrations tend to cause a decrease in product purity, which, however, can be maintained for small feed composition changes by adjusting the feed-to-permeate pressure ratio. In most refinery membrane applications, however, the major product impurity is methane and this can be allowed to increase slightly in the product without major downstream impact. The flue gas stream contains an amount of CO₂ ranging from 5 % to 35 % depending on the process, the rest being mainly nitrogen and few percentage of oxygen. Whether the CO₂ concentration is always higher than 20 %, the membrane systems can be considered highly flexible. On the contrary, for CO₂ concentration lower than 20 % the membrane operation offers a very low flexibility. A further reduction in CO₂ concentration, in fact, produces a reduction of the driving force with a consequent decrease in CO₂ recovery and in product purity.

The response time of membrane systems is essentially instantaneous and corrective action has immediate results. The start-up time required by the process is extremely short.

The flexibility of the absorption process is moderate. This system, in fact, responds quite well to the changes in the feed composition; however, significant differences in the fraction of the desired specie contained in the feed imply higher solvent flow rate that is strictly related to the size of equipment apart from the absorber. Furthermore, the fact that the feed stream contains oxidizing compounds (oxygen or sulfur dioxide) induces major problems of amine deactivation and promotes corrosion.

The PSA process shows a great ability to maintain purity and recovery under changing conditions. The process is self-compensating and even relatively large changes in feed impurity concentrations have little impact on performance. As the concentration of a feed impurity increases, its partial pressure increases, increasing also the amount of the impurity which will be adsorbed.

The purity can be maintained constant by a simple cycle time adjustment. The response time to variations is rapid but not abrupt, generally requiring 5–15 min for responding to a step change in feed quality. The new steady-state upon restart following shutdown is reached in about 1 h.

The cryogenic process has very low flexibility because changes in the concentration of the lower boiling components of the feed affect the product purity directly. Recovery is not strongly affected. Response time is not as rapid as for PSA or membrane systems. Start-up is 8–24 h depending on the procedure used.

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Fluidized Bed Membrane Reactors

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A fluidized bed membrane reactor, also indicated as membrane-assisted fluidized bed (MAFBR), is an integrated reactor where membranes (in form of tubes, hollow fibers, or planar modules) are immersed in a fluidized bed of catalyst particles. Typical example of MAFBR for hydrogen production is reported in (Gallucci et al. 2010a) and consists in a bundle of hydrogen-selective membranes immersed in a catalytic bed operated in bubbling regime. The use of fluidized bed membrane reactors makes possible the reduction of bed-to-wall mass transfer limitations, but also allows operating the reactor at a virtually

isothermal condition (due to the movement of catalyst). This possibility can be used for operating the autothermal reforming of hydrocarbons inside the membrane reactor. In fact, as indicated by Tiemersma et al. (2006), the autothermal reforming of methane in a packed bed membrane reactor is quite difficult due to the hot spot at the reactor inlet which can melt down the membrane. This problem is completely circumvented in fluidized bed membrane reactors. In this case both autothermal reforming and hydrogen recovery can be performed in a single reactor.

According to Deshmukh et al. (2007) the main advantages of the MAFBR can be listed as follows:

- Negligible pressure drop, which allows using small particle sizes resulting in limited internal mass and heat transfer limitations (higher effectiveness factors)
- (Virtual) Isothermal conditions
- Flexibility in membrane and heat transfer surface area and arrangement of the membrane bundles
- Improved fluidization behavior as a result of:
 - Compartmentalization, i.e., reduced axial gas back-mixing.

Reduced average bubble size due to enhanced bubble breakage, resulting in improved bubble to emulsion mass transfer.

MAFBR for hydrogen production also circumvent the bed-to-wall mass transfer limitations affecting packed bed membrane reactors. It has been demonstrated that higher membrane fluxes (possible with nowadays membranes) will cause a significant increase of the concentration polarization in packed bed membrane reactors, even in membrane tubes with a diameter as small as 1 cm. By using the MAFBR, the membrane area required for a fixed hydrogen flux can be decreased by 50 % if compared with packed bed reactors (Gallucci et al. 2010a).

Even though Rahimpour and coworkers often used fluidized bed membrane reactor for distributive hydrogen feeding in methanol reactors (see Rahimpour and Lotfinejad 2008), most of the literature has focused on pure hydrogen

production through Pd-based membranes (see among others Adris et al. 1991; Prasad and Elnashaie 2002) and on autothermal reforming reactions (see a.o. Grace et al. 2001; Gallucci et al. 2010b).

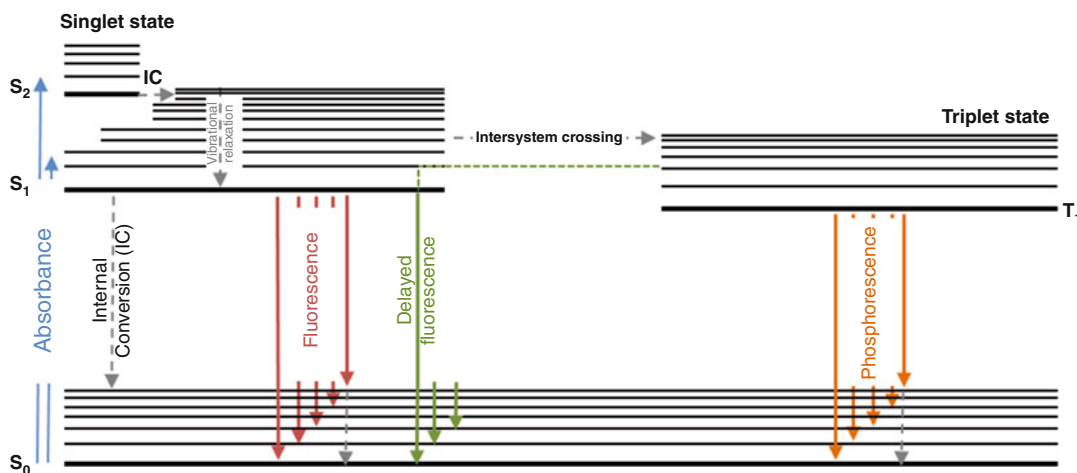
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Fluorescence

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Fluorescence is a photoluminescence process which consists of the emission of photons along the de-excitation of molecular species from the excited state S_1 to the ground state S_0 . The loss



Fluorescence, Fig. 1 Perrin-Jablonski diagram schematizing the radiative (*bold lines*) and non-radiative (*dashed lines*) de-excitation processes

of energy by molecular species in the excited state may occur through radiative processes (i.e., with photon emission) or via nonradiative (i.e., without photon emission) de-excitation mechanisms, as schematized in Fig. 1.

Radiative de-excitation may occur via fluorescence or phosphorescence emission, whereas nonradiative de-excitation may occur through intersystem crossing or internal conversion mechanisms, which may be coupled to additional energy losses through vibrational relaxation to the lowest energy level. The former corresponds to electronic transitions between states with the same multiplicity whereas intersystem conversion implies an electronic transition between isoenergetic vibrational levels of different multiplicity (singlet to triplet states) (Valeur 2002). Electronic transitions from triplet state to the ground state are possible through radiative processes, such as phosphorescence or delayed fluorescence (upon returning to the excited singlet state).

Nonradiative de-excitation results from interactions between the excited species and other molecules in their close proximity (intermolecular processes) where energy loss is consequence of heat release due to molecular

collision, or electron, proton, and energy transfer. Also, it may involve excited state chemical reactions, leading to the formation of different molecular species (excimers or exciplexes). These intermolecular de-excitation mechanisms are responsible for fluorescence quenching, which is characterized by a fast electronic decay to the ground state and therefore it may compete with fluorescence, leading to a decrease of the fluorescence quantum yield, ϕ_F . Hence, ϕ_F expresses the ability of an excited molecule to decay to the ground state through fluorescence radiative process and can be determined by the equation

$$\phi_F = \frac{k_r}{k_r + k_{nr}}$$

where k_r and k_{nr} are the rate constants for radiative and nonradiative deactivation processes in the singlet state (Valeur 2002), respectively.

Fluorescence emission is highly sensitive to the intrinsic physicochemical characteristics of fluorophores and also to changes of its involving media. Indeed, steady-state fluorescence emission spectra acquired upon excitation with randomly oriented light allows at eliciting information about

the excited state molecular events occurring in equilibrium, based on changes in fluorescence intensity or maximum emission shifts (Portugal et al. 2006, 2007; Martinho et al. 2003). The former may be related with the variation of concentration of fluorophores present in the sample but also it may be ascribed to other molecular events such as fluorescence quenching, inner filter effects (e.g., light scattering or reabsorption of emitted light), and chemical reactions with the formation of different species. Instead, the presence of maximum emission shifts to lower (blue-shift) or higher (red-shift) wavelengths may evidence changes in the polarity in the vicinity of the fluorophores. Applied to intrinsic fluorophores of proteins, e.g., tryptophans, these spectral changes may reveal protein folding/unfolding processes (Portugal et al. 2006, 2007).

Fluorescence anisotropy corresponds to the fraction of polarized light emitted by a fluorophore upon excitation with polarized light, as expressed by the following equations (Valeur 2002):

$$r = \frac{\text{Polarized light}}{\text{Total light}} = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = \frac{I_{VV} - I_{VH} \times G}{I_{VV} + 2 \times I_{VH} \times G}$$

$$G = \frac{I_{HV}}{I_{HH}}$$

where $I_{\parallel}$ represents the fraction of emitted parallel polarized light (I_{VV} and I_{HH}) and $I_{\perp}$ corresponds to the fraction of emitted perpendicular light (I_{VH} and I_{HV}).

Fluorescence anisotropy relates with the depolarization of light in the excited state due to the rotational freedom of the fluorophores. Therefore, fluorescence anisotropy may provide information about constraints imposed on the fluorophore by the system, molecule, or matrix where it is included in, through detection of changes of the fluorophore rotational ability (Lakowicz et al. 1983). Hence, the increase of fluorescence anisotropy may be ascribed to a decrease of fluorophore mobility. Recalling the example of tryptophan, changes of its mobility within the

protein chain may report protein folding/unfolding processes or changes of protein molecular flexibility, e.g., caused by protein adsorption/desorption mechanisms (Portugal et al. 2006, 2007).

The emission fluorescence spectra obtained in steady state correspond to the contribution of all the fluorescing species present in the system under analysis that are able to absorb energy at the selected excitation wavelength. The ability to discriminate the contribution of each fluorescing species depends largely on the system complexity, but it may be possible through determination of their individual fluorescence decay times (Beechem and Ludwig 1985). Fluorescence decay times may be elicited by fitting of adequate functions, e.g., sum of exponentials (where each parcel corresponds to the contribution of the single fluorescing species) described below (Beechem and Ludwig 1985; Valeur 2002).

$$I(\lambda, t) = \sum_i a_i e^{-t/\tau_i}$$

where $I(\lambda, t)$ is the variation of fluorescence emission along the time, a_i corresponds to the amplitude of the decay, t and τ_i are the measuring time and the fluorescence decay time, respectively.

Due to the high sensitivity of fluorescence emission and fluorescence decay times to changes of temperature, pH, ionic strength, and solvent properties (e.g., polarity, dielectric constant) and the presence of fluorescence quenchers in the surrounding media, some fluorophores have been efficiently used as fluorescence probes for monitoring of membrane-based processes. Fluorescence spectroscopy has been used toward the development of membrane materials less prone to fouling, through inspection of fluorophores adsorbed at the material surface (Gironès et al. 2006). Also, it can be used for monitoring the performance of membrane permeation processes (Crespo et al. 1999; Galinha et al. 2012).

Furthermore, it has been used to obtain a better comprehension about the impact of membrane processes on the structural and functional properties of biomolecules, e.g., proteins, using tryptophan as the structural probe. Using a fluorescence monitoring approach which combined the complementary information provided by steady-state fluorescence, fluorescence anisotropy, and time-resolved fluorescence it was demonstrated that under specific processing conditions (e.g., transmembrane pressure, membrane molecular weight cutoff, membrane chemistry) membrane permeation may induce irreversible changes of protein structure and function (Portugal et al. 2006).

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Fluorescence Excitation-Emission Matrix (EEM)

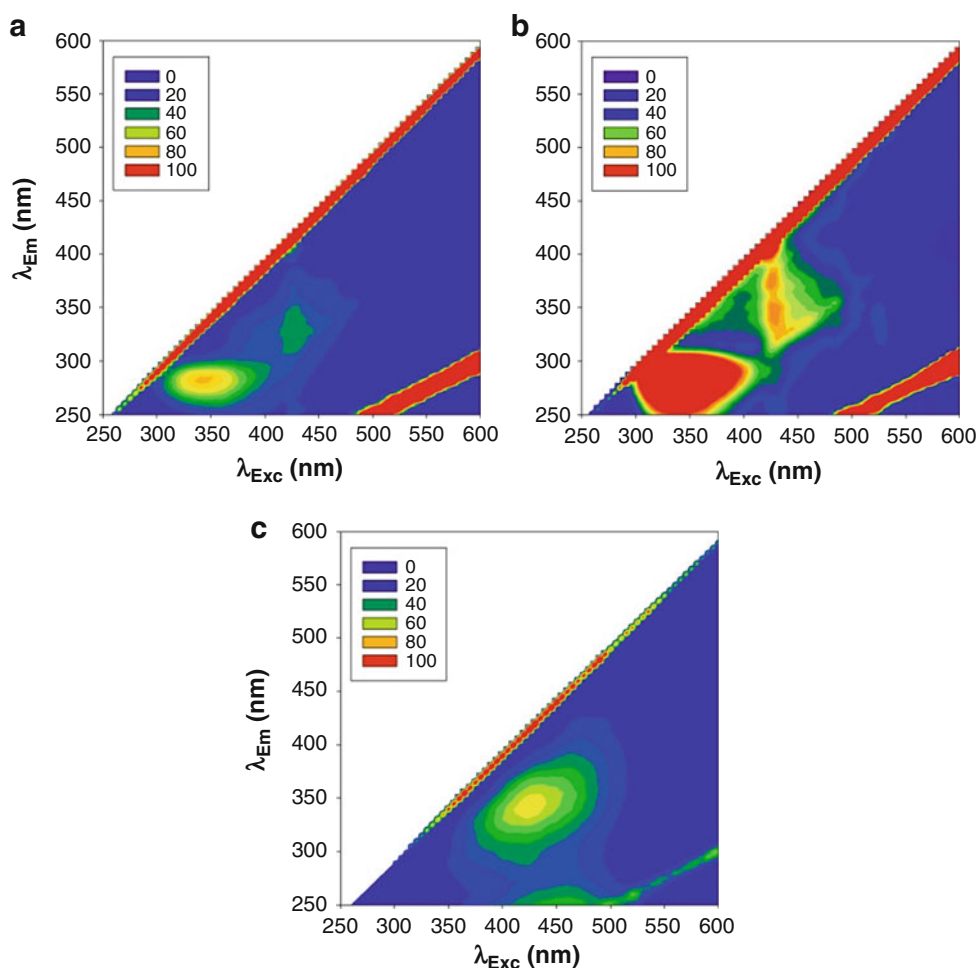
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The fluorescence emission of molecular species depends on their intrinsic physicochemical characteristics and on their interactions with the surrounding media. Therefore, fluorescence emission is extremely sensitive to changes of the environmental conditions in the fluorophore's vicinity (e.g., pH, temperature, presence of fluorescence quenchers, solvent properties). Together, these factors define the period during which a fluorophore remains in the excited state, i.e., fluorescence lifetime, and the magnitude of each radiative and non-radiative de-excitation process component, through which the fluorophore decays to the ground state (the lowest energy level).

This dependency relation limits the use of fluorescence spectroscopy for quantitative purposes, but simultaneously it explains the potential of this technique to provide information about the system status using single or multiple fluorescence probes (fluorophores). The information about the molecular events occurring in the system may be obtained based on changes of the fluorescence emission of a single probe, through acquisition of the fluorescence signal at only one pair of excitation-emission wavelengths, generally corresponding to the specific maximum emission of the fluorophore. Alternatively, it may be elicited by selecting one of the fluorescence signal dimensions (excitation or emission wavelength) and scanning the other within the range of interest. Despite sensitive, this approach may hamper a complete system description since it reports only the media interactions with a single probe, discarding possible additional information captured by other fluorescence probes also present



Fluorescence Excitation-Emission Matrix (EEM), Fig. 1 Fluorescence excitation-emission matrices (EEMs) obtained at different locations of a MBR system

used for wastewater treatment: (a) feed wastewater, (b) activated sludge inside the bioreactor and (c) clarified permeate upon treatment

in the system, emitting in different spectral regions. Thus, a more thorough system characterization can be achieved by scanning simultaneously excitation and emission wavelengths in order to cover a larger spectral region and capture the information provided by each fluorophore present in the system. This 2D fluorescence monitoring approach results in tridimensional fluorescence maps having as coordinates the fluorescence emission intensity, excitation (λ_{Exc}) and emission (λ_{Em}) wavelengths, so-called excitation-emission matrices (EEM), as those illustrated in Fig. 1.

Therefore, EEMs may be regarded as system fingerprints encoding valuable information

concerning the presence of the fluorescence probes in the system (Marose et al. 1998) as well as their interactions with their involving media (Galinha et al. 2011). EEMs are thus a sum of constructive and destructive interferences of the media conditions with the probe intrinsic fluorescence. Constructive interferences are those that contribute to the increase of the fluorescence emission of a specific probe, thus facilitating its detection, such as those resulting from decrease of temperature or solvent polarity. Oppositely, destructive interferences are those that limit the detection of specific fluorescence response. Destructive interferences are quite common in

complex systems being caused by a large diversity of phenomena, such as (1) superimposition of emission spectra from different fluorescent solutes; (2) quenching effects, prompted by molecular species in close proximity to the probe, which interfere in the fluorophore de-excitation process reducing its fluorescence emission component; and (3) inner filter effects, including the re-absorbance of the emitted light by other solutes (e.g., when the absorption spectra of solutes superimpose, at least partially, the fluorophore emission spectra) and light scattering promoted, for instance, by the presence of suspended solids or turbidity.

Although it perturbs the direct measurement of the fluorophores (Galinha et al. 2011; Kobbero et al. 2008) and the access to convoluted data embedded in EEMs, interferences should be regarded as an additional rich source of information that can be disclosed by the use of adequate mathematic tools. Such approach has been applied for the characterization of different water streams (Galinha et al. 2011; Osburn et al. 2012) and for the monitoring of biological and wastewater treatment processes, namely, membrane bioreactors, MBRs (Fig. 1). Fluorescence monitoring has been used aiming to get a better understanding of membrane fouling mechanisms, in order to define adequate strategies, which may allow for the mitigation of fouling problems (Peiris et al. 2010). Mathematical approaches based on the use of multivariate statistical tools, combining principal component analysis (PCA or PARAFAC) and projection to latent structure (PLS) modeling (Galinha et al. 2012) or artificial neural networks (ANNs) (Wolf et al. 2001), allow for establishing relationships between EEMs and relevant process output variables, leading to an accurate prediction of some process performance descriptors (e.g., transmembrane pressure, chemical oxygen demand, total nitrogen, nitrites and nitrates, reaction rates).

2D fluorescence spectroscopy offers the possibility of simple, real-time, and non-invasive monitoring of biological or non-biological processes at different points of the system by using optical fibers. Moreover, it allows accurate prediction of process performance parameters and the potential

anticipation of process problems without the need of the traditional time-consuming analytical methodologies.

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Fluorinated Polymers

► Amorphous Fluoropolymers

Fluoroplastics

► Amorphous Fluoropolymers

Fluxes and Driving Forces in Membrane Separation Processes

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The transport rate of a component through a membrane is determined by the permeability of the membrane and by the driving force. Generally, the flux through a membrane can be described by

$$J = -P \frac{dX}{dz} \quad (1)$$

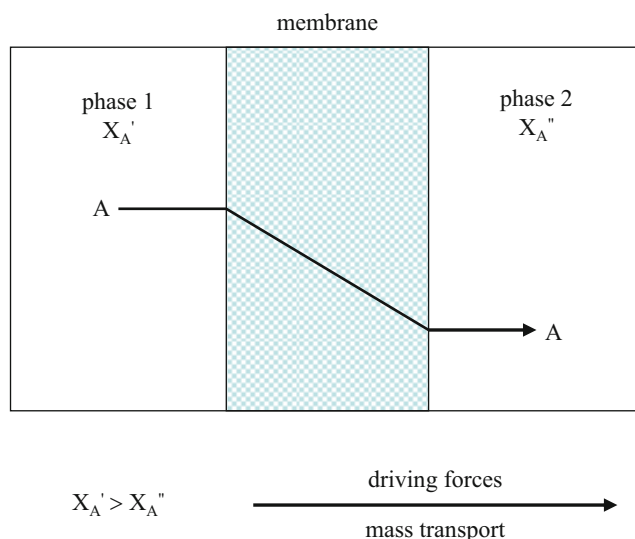
where J is a flux, P is a phenomenological coefficient expressing the permeability of the membrane, and $\frac{dX}{dz}$ is the driving force. The flux through the membrane can be defined as volume flux (J_v) expressed in volume per time ($\text{m}^3 \cdot \text{s}^{-1}$), mass flux (J_m) expressed in mass per time ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), molar flux (J_n) expressed in mole per time ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), electrical flux (J_e) expressed in Faraday per time ($\text{A} \cdot \text{m}^{-2}$), and heat flux (J_q) expressed in heat per time ($\text{J} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$).

Fluxes and Driving Forces in Membrane Separation Processes,

Fig. 1 The schematic diagram of mass transport through a membrane

The driving forces in membrane processes are gradients in the chemical potential, the electrical potential, and the hydrostatic pressure, which could result in a diffusion of individual molecules, a migration of ions, and a convection of mass, respectively. The function of the membrane is illustrated in Fig. 1. The transport of the component A from phase 1 through a membrane into the phase 2 is due to the driving force as shown in Fig. 1.

According to the driving forces, the membrane processes can be classified into the pressure-driven processes (reverse osmosis, ultra- and microfiltration, and gas separation), the concentration gradient-driven processes (dialysis), partial pressure-driven processes (pervaporation), and electrical potential-driven processes (electrolysis and electrodialysis). The main driving forces in the different membrane processes are illustrated in Table 1. It can be seen in Table 1 that the hydrostatic pressure differences are used in micro- and ultrafiltration, as well as in reverse osmosis and gas separation as driving force for the mass transport through the membrane. The mode of transport in micro- and ultrafiltration is convection. However, in reverse osmosis and gas separation, the mode of transport is diffusion, and the actual driving forces are chemical potential and fugacity gradients. The mode of transport in dialysis is diffusion with concentration or activity



Fluxes and Driving Forces in Membrane Separation Processes, Table 1 The driving forces applied in the various membrane separation processes (Strathmann 2001)

Process	Driving force	Transport mode
Microfiltration	Hydrostatic pressure (Δp)	Convection
Ultrafiltration	Hydrostatic pressure (Δp)	Convection
Reverse osmosis	Hydrostatic pressure (Δp)	Diffusion
	Chemical potential ($\Delta \mu_i$)	
Dialysis	Concentration (ΔC)	Diffusion
	Activity (Δa)	
Gas separation	Hydrostatic pressure (Δp)	Diffusion
	Fugacity (Δf_i)	
Pervaporation	Partial pressure (Δp_i)	Diffusion
	Fugacity (Δf_i)	
Electrodialysis	Electrical potential ($\Delta \phi$)	Migration

gradients as driving forces. And an electrical potential gradient in electrodialysis is used to achieve a migration of charged ions across the membrane.

In order to describe the transport processes through membranes, a number of equations which are related to the fluxes of various components to the corresponding driving forces in the form of linear relations are developed as follows:

Fourier's law

$$J_q = -\alpha \frac{dT}{dz} \quad (2)$$

Fick's law

$$J_n = -D \frac{dC}{dz} \quad (3)$$

Darcy's law

$$J_v = -L_p \frac{dp}{dz} \quad (4)$$

Ohm's law

$$J_e = \kappa \frac{d\phi}{dz} \quad (5)$$

Herein T is the temperature, C is the concentration, p is the pressure, ϕ is the electrical potential, α is the heat transfer coefficient, D is the diffusion

coefficient, L_p is the hydrodynamic permeability, and κ is the electric conductivity.

Fourier's law describes the relation between heat transport and a temperature gradient. Fick's law describes the relation between the flux of individual components and a concentration gradient. Ohm's law describes the relation between an electrical current and an electrical potential gradient, and Darcy's law describes the relation between a volume flux and a hydrostatic pressure difference. These two factors should be interlinked: a high driving force yields the high flux and a high rate of foulants deposition on the membrane surface. Therefore, driving forces and fluxes are interdependent in membrane processes.

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Food Packaging

► [Food Packaging, Membranes for](#)

Food Packaging, Membranes for

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Synonyms

[Food packaging; Membrane operations](#)

Food packaging is often defined as a heterogeneous group of boxes, envelops, papers, and coatings that are employed in order to increase foodstuffs shelf life (European Council 1994). This means that any food packaging system aims to avoid/slow down bacterial/fungal

Food Packaging, Membranes for,

Fig. 1 Application of membrane in traditional food packaging, revised from ref. (Figoli et al. 2010)



contamination and deterioration and, at the same time, to ensure the maintenance of properties as firmness, color, and flavor as long as possible.

Nowadays, beside the traditional concept of packaging as impenetrable barrier, novel systems are required, such as *modified atmosphere packaging* (MAP) and *active packaging* (AP). Polymeric membranes, thanks to their unique properties of permselectivity and ability to sustain controlled delivery, can be successfully used for food packaging; indeed, their properties can be exploited for such innovative packaging systems (Figoli et al. 2010), as also shown in Fig. 1. Furthermore, the expertise of membranologists could help to produce food packaging systems from biodegradable nonpolluting sources. In particular, the properties of films produced from *biopolymers* can be improved by well-developed techniques as blending, use of plasticizers, and loading with nanoparticles.

MAP is frequently used in the case of fresh, or minimally processed, respiring, products, like vegetables and fruits. MAP aims at maintaining an optimum gas balance in the package headspace. In particular, a selected ratio between carbon dioxide and oxygen is often required in order to allow living vegetal tissues respiration and survival, at the same time preventing aging and deterioration. The respiratory quotient (RQ) (Cameron et al. 1995) is defined as the optimum balance between O_2 and CO_2 that should be maintained within the package; this value is peculiar of each fruit or vegetable specimen. MAP requires films having specific permselectivity to gases, such as carbon dioxide and oxygen, rather than impenetrable materials. In this case, gas separation membranes can be particularly useful, while membrane materials can be selected, in each case, on the basis of their permselectivity to

oxygen and carbon dioxide. By varying the ratio between polymer and additive concentrations, dense membranes in modified polyether ether ketone (PEEK-WC) and poly- α -pinene (P α P) were reported to match the values required by different products, as apple, Brussels sprouts, carrot, green pepper, and turnip (Torchia et al. 2004).

A wide range of CO_2/O_2 permselectivity values can be obtained by using packaging structures based on biopolymers. These are defined as biodegradable materials that can be decomposed by microorganisms and enzymatic degradation. Starch, cellulose, chitosan, polycaprolactone (PCL), and polylactic acid (PLA) are some examples of biopolymers suitable for food packaging (Mensitieri et al. 2011). In literature, several studies already demonstrated that biopolymers can compete with oil-derived plastics for packaging of different fruit and vegetable species (see for instance ref. Conte et al. 2009; Kantola and Helen 2001; Muratore et al. 2005; Srinivasa et al. 2002). However, hydrophilicity and poor mechanical properties are the main drawbacks for use of biopolymers as food packaging systems. Several strategies, already developed in the field of membrane science and technology, can be useful to improve properties and processability of biopolymers for food packaging, such as use of chemical additives (plasticizers, antioxidants, stabilizers) (Torchia et al. 2004; Abdorreza et al. 2011), blending (Torchia et al. 2004; John et al. 1998; Sarazin et al. 2008), chemical cross-linking (González et al. 2011; Yu et al. 2011), or use of nanofillers (Belbekhouche et al. 2011; Chivrac et al. 2009; Famá et al. 2011; Hu et al. 2011; Li et al. 2011).

Active releasing packaging systems are used to control the delivery of specific substances to the

packed product. Membranes loaded with specific substances, coated on the surface, or entrapped in the polymeric matrix can be useful in this case, similar to what already developed in the medical field (Baker 2002). Membranes can be used to sustain the controlled delivery of antimicrobial substances, such as allyl isothiocyanate (AITC) (Lee et al. 2008) or oxalic acid (Figoli et al. 2004). Active release can be also combined with use of biopolymers. Films based on starch, corn zein, and PLA can be used for delivery of lysozyme, nisin, and natural antimicrobial compounds (Torchia et al. 2004); literature reports several other interesting examples of biopolymer-based films as active packaging systems (Atarés et al. 2011; Chana-Thaworn et al. 2011; Gemili et al. 2009; Sánchez-González et al. 2011). Microencapsulation is another strategy for controlled delivery. It has been shown that it can be used coupled to traditional packaging materials or biopolymers for active packaging systems releasing natural antimicrobials (Guarda et al. 2011) or aroma compounds (Marcuzzo et al. 2010).

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Food Processing by Membrane Operations

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Food processing consists of transformation of raw ingredients into food, or food itself into other forms. Food processing typically starts with clean, harvested crops or butchered animal products and uses them to produce safe and attractive products – along the food chain, down to the consumer at home (Marsh and Angold 2004). Various unit operations are part of the current practice, which rely on either thermal processing or mechanical work: the former are less appropriate to heat-labile items and are also characterized by poor thermodynamic efficiency. Mechanical work is, to advantage, applied in membrane-based processes: they take advantage of a physical barrier (i.e., a porous membrane or filter) to separate particles

from a fluid based on their size and shape and resort to high pressure and tailor-made membranes with specific pore sizes. The pore size distribution allows indeed different possibilities in terms of separation to be attained – via microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (sorted by decreasing pore size) (Drioli et al. 2011).

Membrane processing has met with industrial success in clarification and concentration of liquid foods because it operates at room temperature, entails low energy consumption, and is highly preformant with regard to a wide range of contaminants – besides scaling up easily (Sant’Anna et al. 2012); it may also increase yield, and its high selectivity can be taken advantage to improve control (Drioli et al. 2011). Membranes are able to remove sediments, microorganisms, and large-sized compounds; they offer indeed an efficient way to gain superior quality and safety without disturbing the basic sensory profile of a food product. As major disadvantages, one should outline high hydraulic pressure drops, limited maximum attainable concentration, and concentration polarization – especially in media with high loads of organic compounds (Petrotos et al. 2010).

Microfiltration separates suspended particles, typically from 0.1 to 10 μm (thus including bacteria); for sterilization purposes, 0.4–0.6 μm membranes in dead-end and cross-flow filtration modes are recommended. Permeate fluxes of the order of 100,000 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ are typically observed when processing (clean) water; liquid foods usually reduce such a permeate flux to 100–200 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, owing primarily to viscosity, fouling, and concentration polarization (Accomazzo et al. 1988).

Ultrafiltration resorts to membranes with pore sizes in the range of 0.1–0.001 μm ; it is typically intended for removal of high molecular weight substances, colloidal materials, and polymeric molecules of organic or inorganic nature. Ultrafiltration is a cross-flow separation process – i.e., the liquid feed flows tangentially along the membrane surface with a pressure drop across it, causing part of that stream to percolate the membrane (thus producing a permeate). The type and amount of species left in the remaining stream (retentate) depend on the characteristics of the membrane

and the operating conditions, as well as the composition of the original feed. Optimum design and operation should take into account the flow velocity, the pressure drop, the power consumption, the rate of membrane fouling, and the module cost. Since only high molecular weight species are removed, the differential in osmotic pressure across an ultrafiltration membrane is usually negligible (Accomazzo et al. 1988).

Nanofiltration is a ► [cross-flow filtration](#) technology, usually listed between ultrafiltration and reverse osmosis; the nominal pore size of the membrane is typically ca. 1 nm, but the ► [molecular weight cutoff](#) – which is typically less than 1,000 Da, rather than the nominal pore size – is to be used for a more meaningful characterization. Transmembrane pressures can go up to 3 MPa, which require powerful pumping equipment; furthermore, nanofilter membranes are quite susceptible to scaling and fouling, so such modifiers as antiscalants are often required.

Finally, reverse osmosis goes one step further in filtration and allows separation of small dissolved molecules in the Angstrom range; this includes salts, sugars, and organic acids. The only driving force for this process is the osmotic pressure difference between the solutions lying on the two sides of the permeable membrane. The cross-flow configuration allows the membranes to self-clean continually; further advantages encompass relatively low hydraulic pressure and easy scale-up (Sant'Anna et al. 2012).

Membrane contactors represent another approach to membrane operations in food processing – where separation does not rely specifically on the membrane acting as selective barrier, but is instead based on phase equilibria. Hence, mass transfer between phases is promoted without dispersing one phase into the other, and such disadvantages as flooding at high flow rates, unloading at low flow rates, requirement for emulsified state and density differences, and high interfacial area are dramatically alleviated. In principle, all traditional stripping, scrubbing, absorption, evaporation, distillation, crystallization, emulsification and liquid-liquid extraction, as well as enzymatic catalysis can be carried out

following this configuration. This type of contactor technology has found applications in purification of water, wine fermentation, protein extraction, and beverage carbonation (Stanojević et al. 2003).

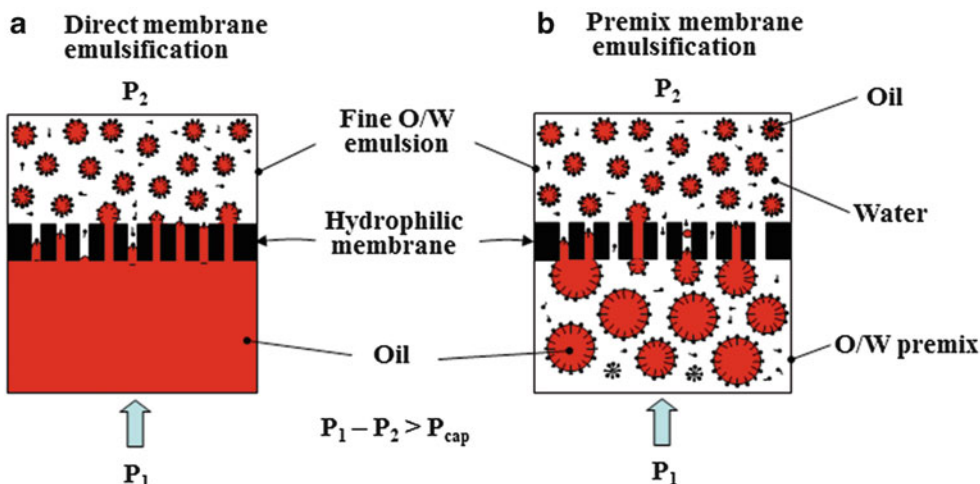
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Formulation by Membrane Emulsification

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Membrane emulsification (ME) is a process of forming emulsion by passing a pure dispersed phase or pre-emulsion through a microporous membrane (Fig. 1). The most commonly used membranes for ME are Shirasu porous glass (SPG) membrane and microsieve membranes. In direct ME, fine droplets are produced at the membrane/continuous phase interface by injecting a



Formulation by Membrane Emulsification, Fig. 1 Two different approaches used to obtain fine droplets of oil-in-water emulsion in membrane emulsification

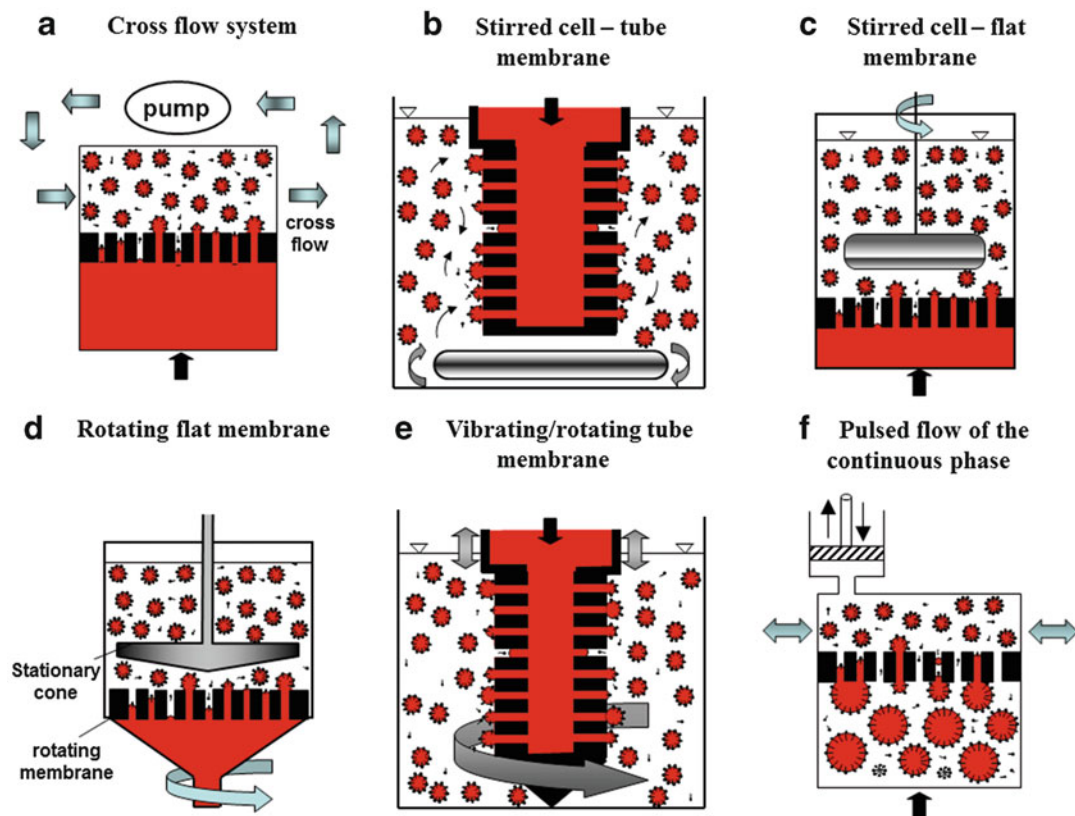
(ME): a “bottom-up” approach (direct ME); b “Top-down” approach (premix ME)

pure liquid (the dispersed phase) through the membrane into a second immiscible liquid (the continuous phase) (Nakashima et al. 1991). The dispersed phase should not wet the membrane wall, i.e., hydrophobic and hydrophilic membranes are used to produce water-in-oil and oil-in-water emulsions, respectively. At low trans-membrane fluxes, uniform droplets can be formed without applying any shear on the membrane surface, solely by the action of interfacial tension (Kukizaki 2009). In order to achieve commercially significant throughputs in ME, the shear stress is applied at the continuous phase/membrane interface, usually by cross flow or stirring (Fig. 2a–d). Cross-flow systems are easy to scale up and can offer a continuous operation and constant shear stress along the membrane surface. Stirring systems are operated batchwise and do not provide constant shear stress on the membrane surface, but are easier to operate because a closed loop recirculation of the continuous phase stream is not needed and a batch size can be very low, just 10 mL or even less.

The shear stress can also be generated by a dynamic membrane (Fig. 1e) or pulsed flow (Fig. 1f), in which case the droplet detachment from the membrane surface is facilitated by

rotating (Vladislavjević and Williams 2006) or vibrating (Holdich et al. 2010) the membrane within the otherwise static continuous phase or providing periodic flow pulsations in the continuous phase (Holdich et al. 2013). In the dynamic and pulsed flow membrane systems, the shear stress on the membrane surface is decoupled from the cross-flow velocity, and consequently, sufficiently high shear stress can be achieved at any cross-flow velocity, and emulsions with high dispersed phase concentrations can be produced in a single pass through the module.

In the dripping regime, the droplet size is determined by a balance between the shear force and the capillary force. The size of the droplets produced is mainly affected by the microstructure of the membrane (the pore size distribution, pore shape, and pore spacing), transmembrane flux, surface shear stress, physical properties of the continuous and dispersed phase, and emulsion formulation. Surfactant molecules must not adsorb to the membrane surface, and thus, cationic surfactants must not be used in association with negatively charged membrane (such as SPG membrane and oxidized silicon microsieves) (Nakashima et al. 1993). The transmembrane pressure should not exceed ten times the capillary



Formulation by Membrane Emulsification, Fig. 2 Different ME systems used to control shear stress on membrane surface (Vladisavljević and Williams 2005)

pressure and the shear stress on the membrane surface is usually in the range from 2 to 10 Pa (Vladisavljević et al. 2004). The droplet size is typically two to ten times higher than the pore size and decreases with increasing the shear stress on the membrane surface.

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Forward Osmosis (FO)

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In literature, osmotic pressure-driven membrane processes are known as direct osmosis (DO) or forward osmosis (FO). FO dating back to the early 1960s is a membrane contactor process that utilizes osmotic pressure difference ($\Delta\pi$) across the membrane for water transport through a semipermeable membrane (Cartinella et al. 2006; Cath et al. 2006) than a hydraulic pressure as in RO. The osmotic pressure difference across the membrane arises from the use of concentrated solution called draw solution (DS) on the permeate side of the membrane (Fig. 3a). Apparently FO may be a viable and sustainable alternative to thermal-driven (membrane distillation) and pressure-driven (reverse osmosis) concentrating methods, which are highly energy intensive, hence very expensive. In the presence of natural sources of concentrated DS, e.g., seawater, FO can be very attractive due to its significantly lower energy demand for pumping (Tang et al. 2010). The equation below is generally used to describe water transport in FO:

$$J_w = A(\sigma\Delta\pi - \Delta P) \quad (1)$$

where J_w is the water flux, A the water permeability constant of the membrane, σ the reflection coefficient, and ΔP is the applied pressure. For FO, ΔP is zero.

Currently many researchers are focusing on the use of FO for different applications, and remarkable progresses are observed in optimizing the process through testing different DS, configurations, and development of model equations that could best explain the phenomena.

Hence, FO is reemerging as low-energy demanding membrane operation ($<30 \text{ kWh/m}^3$) (Beaudry et al. 1999) for dehydration of aqueous solution

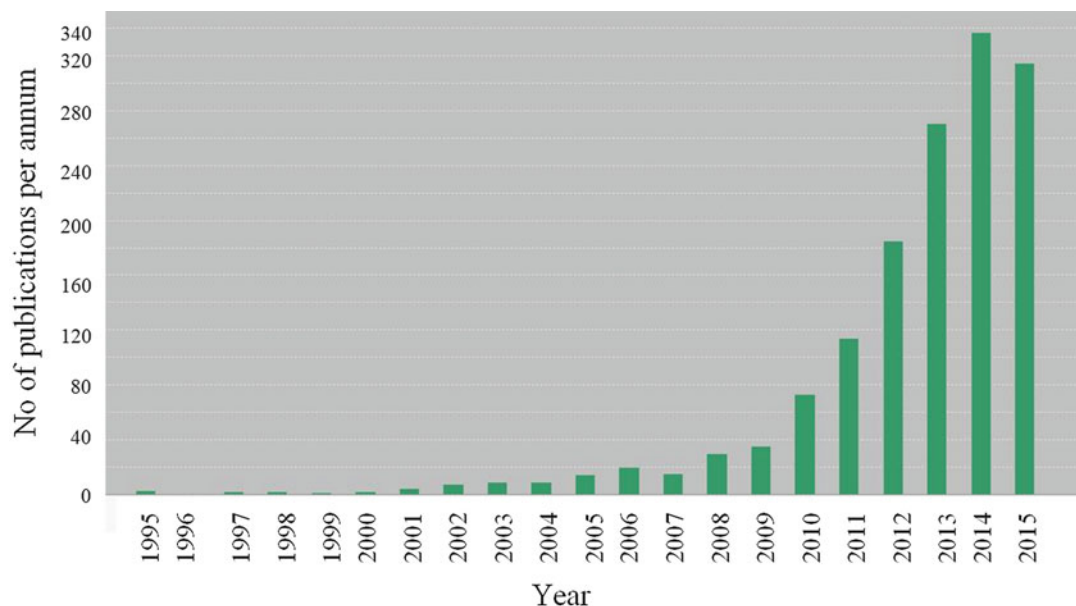
(Klaysom et al. 2013), seawater desalination (McCutcheon et al. 2005), wastewater treatment and concentration of diluted streams (Holloway et al. 2007), food processing (Petrotos et al. 1998), removal of trace organic matter (Cartinella et al. 2006), and for use in membrane bioreactor (Zhang et al. 2012). As shown in Fig. 1, there is an exponential rise in the number of FO-related publications in the last 5 years. Similarly, the number of patents released from 2009 to 2014 is significantly high (Fig. 2), providing a pertinent prospect to its application in various fields.

The following are summaries of the range of potential advantages of FO process:

- Requires low/no hydraulic pressure since it is an osmotically driven process.
- Low energy consumption, thereby lowering costs, if suitable draw solutes and their regeneration methods can be economically and technically developed.
- Energy can be harvested from the mixing of freshwater and saline water by pressure-retarded FO (PRO).
- Membrane fouling in FO is relatively low and more reversible and can be minimized by optimizing the hydrodynamics.
- Numerous contaminants can be effectively rejected by the FO process.
- Has the potential to help achieve high water recovery, which reduces the volume of desalination brine, a major environmental concern for current desalination.
- In the food and pharmaceutical processing, FO can maintain color, taste, aroma, and nutrition of the feed.
- In the medical applications, FO can help in the controlled release of drugs with low oral bio-availability in a controlled manner by osmotic pumps.

FO Membranes, Membrane Configurations, and Modeling Membrane Transport

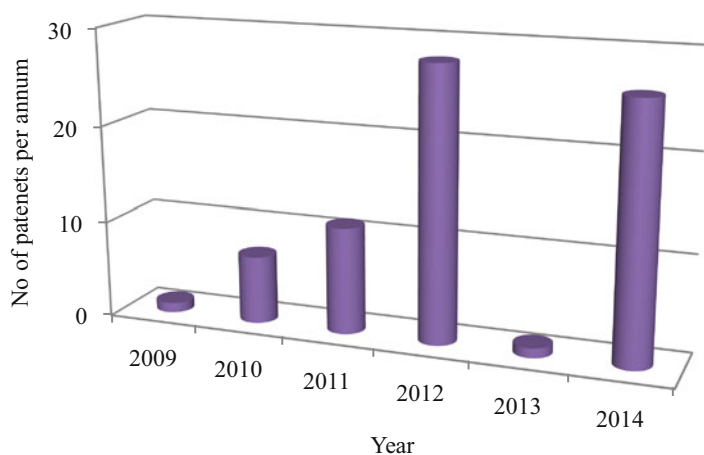
Except for a few authors such as McCutcheon et al. (2005) which used a thin-film composite



Forward Osmosis (FO), Fig. 1 The number of publications excluding patents retrieved from web of science between the year 1996 and 2015 using the keyword “forward osmosis.” [http://apps.webofknowledge.com/CitationReport](http://apps.webofknowledge.com/CitationReport.do?product=UA&search_mode=CitationReport&SID=T1GuVqD4QDADmHXOVbu&page=1&cr_pqid=1&viewType=summary).

[do?product=UA&search_mode=CitationReport&SID=T1GuVqD4QDADmHXOVbu&page=1&cr_pqid=1&viewType=summary](http://apps.webofknowledge.com/CitationReport.do?product=UA&search_mode=CitationReport&SID=T1GuVqD4QDADmHXOVbu&page=1&cr_pqid=1&viewType=summary)

Forward Osmosis (FO), Fig. 2 Number of patents related to FO from 2009 to 2014 retrieved from <http://worldwide.espacenet.com/> using the key word “forward osmosis”



polyamide membrane, most publications are based on cellulose or cellulose derivate (cellulose acetate) membranes mainly from Hydration Technology Inc. In addition, in most cases reverse osmosis (RO) was used to reconcentrate the DS which gets diluted in the course of FO.

Of the different membrane modules, spiral wound modules are one of the most common

packing configurations in the membrane industry. However, it cannot be used in its current design for FO because a liquid stream cannot be forced to flow on the support side (inside the envelope) (Cath et al. 2006). Hence, for a continuous FO operation, flat-sheet membrane and specially designed spiral wound membrane are used. Although applied in limited number, tubular

membranes are also very suitable for continuous FO processing since they are self-supported, can be fabricated easily, and allow free flow of liquid on both sides of the membrane.

There are a number of papers discussing the transport phenomena in FO process in particular related to solution physicochemical properties, concentration polarization, and membrane fouling. For detailed reading, the reader is referred to Tang et al. (2010), McCutcheon and Elimelech (2006), Tan and Ng (2008), and Zhao and Zou (2011).

Draw Solutions

In FO process, a concentrated solution on the permeate side of the membrane is the source of the osmotic driving force. In literature, various names are given to this solution including: draw solution, osmotic agent, osmotic media, driving solution, osmotic engine, sample solution, or brine (Cath et al. 2006). The main criterion for selecting the type of draw solution (DS) is its potential to create higher chemical potential than the feed solution.

The DS and related osmotic pressures in the FO process are important factors influencing overall process performance. Many researchers used salt solution as DS (Cartinella et al. 2006; Cornelissen et al. 2008; Yong et al. 2012), while in some cases sugars or ammonia–carbon dioxide (McCutcheon et al. 2005) solutions were used. According to Lutchmiah et al. (2014), based on publication from 2005 to 2013, 40 % of the cases utilized NaCl as DS. This is mainly attributed by its high solubility (Cath et al. 2006), low cost (Achilli et al. 2010), and relatively high osmotic potential. The same author indicated that 12 % used MgCl_2 , 8 % sugars, 10 % sulfates, and other 7 % used magnetic nanoparticles, real wastewater, carbonates, etc. In addition to these, seawater has frequently been used as a DS (Cath et al. 2010). However, its use was mostly affected by abundant presence of particles and microorganisms which may foul the subsequent system used to reconcentrate the DS (in closed-loop systems) or cause fouling/biofouling in the FO unit, hampering performance.

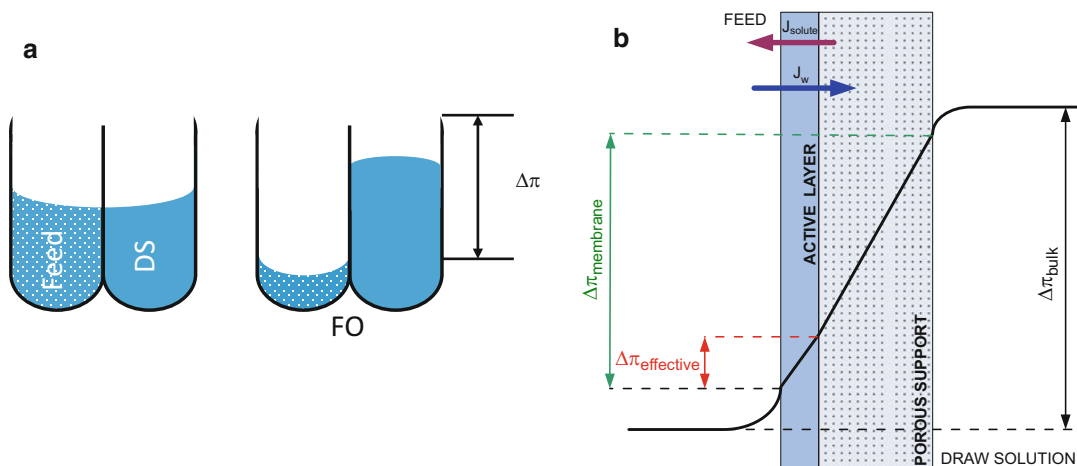
Concentration Polarization and Membrane Fouling

Unlike pressure-driven membrane process, in FO there are both dilutive and concentrative polarization effects that result in a lower-than-expected water flux. Furthermore, the concentration polarization could be either external which occurs near the surface of the active layer and the porous support layer or internal which occurs inside the substructure of porous support layer. As a result, the process is always accompanied by great reduction from the bulk osmotic pressure ($\Delta\pi_{\text{bulk}}$) to the effective osmotic pressure ($\Delta\pi_{\text{effective}}$) as shown in Fig. 3b.

External Concentration Polarization

When the process is in FO mode of operation, i.e., feed solution facing the active side of the membrane, there is accumulation of solute that is rejected by the membrane. This will result in the phenomena of concentrative external concentration polarization (ECP). At the same time, the DS in contact with the permeate side of the membrane gets diluted by the permeating water at the permeate–membrane interface resulting in dilutive external concentration polarization (ECP). Due to these phenomena, the effective osmotic driving force near the membrane is significantly lower than the bulk (apparent) osmotic pressure (Cath et al. 2006).

Interestingly, several studies have shown that fouling induced by ECP in FO in most part is reversible due to low foulant compaction as a result of the negligible hydraulic pressure gradient. Therefore, FO holds a great potential to treat wastewater (Lutchmiah et al. 2014), including wastewater with high fouling propensity (Cicci et al. 2013; Karaouzas et al. 2011). The main strategy utilized to reduce the effect of ECP is increased turbulence or cross flow velocity. Moreover, recovering FO membrane performance was possible using simple osmotic back flush, after it is fouled. For example, an intermittent osmotic back flush has given the possibility to use a single FO membrane over several cycles bringing the total membrane use to 172 h, during the treatment of vegetation wastewater (Gebreyohannes



Forward Osmosis (FO), Fig. 3 Water flows in FO system where (a) water diffuses to the more saline side of the membrane due to osmotic driving force under approximately zero hydraulic pressure and (b) the course

of bulk osmotic driving force reduction to effective osmotic driving force due to concentration polarization phenomena

et al. 2015). This is an important savings in lifetime, compared to the complete performance loss observed in various pressure-driven membrane operations. The FO fouling is generally more pronounced when the porous support layer is facing feed solution, since this orientation is prone to sever internal pore clogging.

Internal Concentration Polarization

The asymmetric FO membrane consists of a dense active layer and a porous support layer, which adds a more complex situation of concentration polarization in FO. In FO applications, where the active layer of the membrane faces the feed solution and the porous support layer faces the DS, there is also dilutive internal concentration polarization (ICP) within the porous substructure. This phenomenon happens when water diffuses through the active layer; the DS within the porous substructure becomes diluted, hence dramatically reduced effective osmotic driving force. Unlike the external concentration polarization, playing with the hydrodynamic condition will not alleviate the problem of ICP. Thus, an engineered solution for reduced internal concentration polarization is optimization of the thickness,

porosity, and tortuosity of the porous substructure (Cornelissen et al. 2008). It is worth noting that compared to ECP, ICP has a more prominent effect in significantly reducing the effective driving force across the dense layer from the bulk osmotic difference.

Promising Application Areas

FO has been studied for a number of applications including commercial applications, in the water and wastewater treatment (e.g., extraction bags) and in the pharmaceutical industry (e.g., osmotic pumps), seawater/brackish water desalination, food processing, drug delivery, and electric power generation. For instance, FO was used to concentrate an oily wastewater from olive millings after removing courser particles in two different configurations. In the first case the pre-filtered wastewater directly fed to the FO process, while in another case permeate of biocatalytic membrane reactor was used as feed. In both cases, FO helped to reduce up to 70 % of the initial volume while completely rejecting all pollutants in the course of reclaiming purified water and pharmacologically important compounds. As a

Forward Osmosis (FO), Table 1 Examples of industrial plants that employed FO process

Stream	Plant name/location	Water recovery	DS	Pollutant rejection (%)
Landfill leachate (Osmotek Inc. 2003)	Coffin Butte Landfill, Corvallis, Oregon	RO: DS and water 92 %	NaCl	99
Direct potable reuse for advanced life-support systems (Beaudry et al. 1999)	DOC NASA long mission life-support system	–	NaCl	Direct potable reuse
Concentration of digested sludge liquids (Holloway et al. 2007)	Truckee Meadows Water Reclamation Facility, Reno, Nevada	RO	NaCl	87–99
Hydration bags (Hydration Technologies Inc. n.d.)	Hydration Technology Inc.	–	Edibles, e.g., sugar, beverage powder	Free of microorganism, macromolecules, and ions

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result it reduced the size of downstream process required to further fractionation and concentration of the recovered pharmaceutically interesting compounds.

Table 1 gives summary of industrial practices on the use of FO process in various fields. It is worth noting that in most wastewater treatment applications, FO is used as a high-level pretreatment step before an ultimate purification step. An exception for this is a hydration bag, which serves as a final treatment step to produce potable water from wastewater.

Concluding Remark

Regardless of the limited presence of robust membranes and membrane modules for FO, fundamental research on FO and the development of new applications of FO are growing fast. However, the following points need to be addressed to have a reliable commercial success:

- Development of new membranes in both flat-sheet and hollow fiber configurations: The development needs to orient in the production of membrane and modules with high water permeability, high solute rejection, limited ICP, high chemical and mechanical stability,

and high-density packing methods for well-performing flat-sheet FO membranes.

- Development of DS: Most desirable DS needs to induce high osmotic pressure, requires low energy for reconcentration, and must be easily separable from the product freshwater and nonreactive with low or no toxicity.

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Forward Osmosis Membrane Reactor

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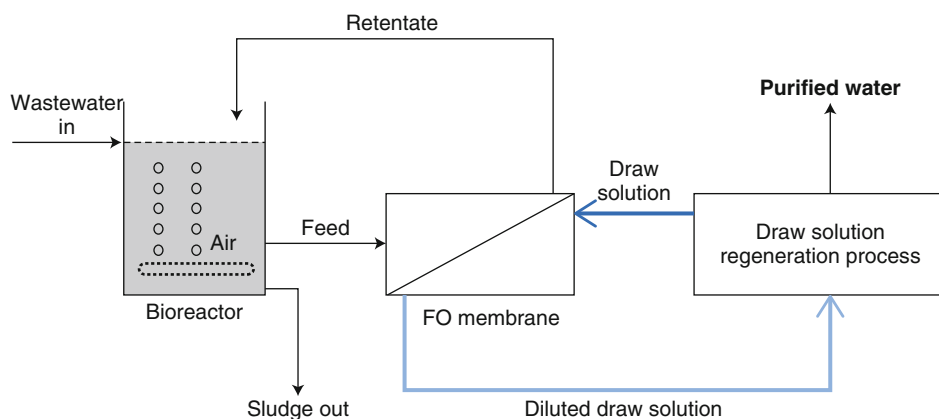
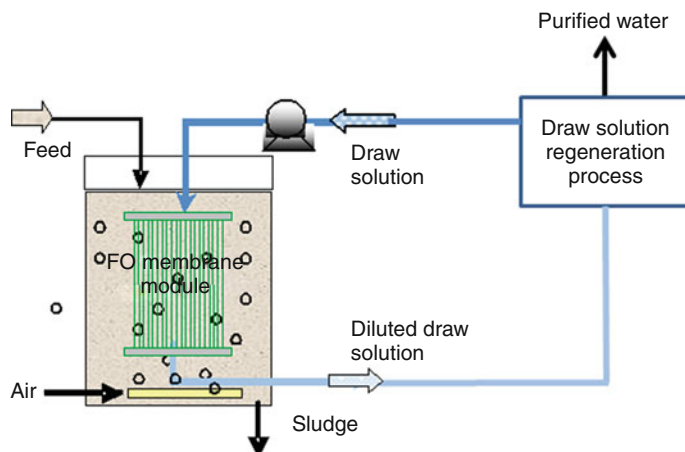
Introduction

The forward osmosis membrane bioreactor (FOMBR) is a new type of membrane bioreactor (MBR) technology, which combines two basic processes – biological degradation of organic wastes and membrane separation using forward osmosis (FO) – into a single process for various wastewater treatments (Zhang et al. 2012). Specifically, in a FOMBR, suspended solids and microorganisms responsible for biodegradation are separated from the treated water using a FO membrane module, where water is extracted from the mixed liquor through a semipermeable FO membrane to a high osmotic pressure draw solution (Achilli et al. 2009). The output from the FOMBR is a mixture of treated water permeate and the draw solution. A posttreatment step, such as reverse osmosis (RO) or membrane distillation (MD), can be used to produce purified water and to regenerate the draw solution.

Compared with conventional MBRs, where pressure-driven membrane filtration units are used, the FOMBR enjoys important advantages including potentially lower energy requirement and better water quality, because the separation does not entail the use of hydraulic pressure, and the salt-rejecting dense membrane is an absolute barrier to suspended solids and also retains organic species. In addition, the use of the dense membrane allows retention of recalcitrant organics which are eventually degraded, as

Forward Osmosis Membrane Reactor,

Fig. 1 Submerged FOMBR



Forward Osmosis Membrane Reactor, Fig. 2 Side-stream FOMBR

organic retention time (ORT) can be significantly longer than the hydraulic retention time (HRT). A greatly enhanced removal of micropollutants is also expected, which is a distinct advantage if the effluent is considered for reclamation and reuse.

Configurations of FOMBR

Similar to conventional MBRs, the FOMBR can be operated under two configurations. One is the submerged FOMBR as shown schematically in Fig. 1 and the other is side-stream FOMBR, as illustrated in Fig. 2 (Yap et al. 2012). In both

configurations, the driving force for water transfer is the osmotic pressure gradient across a salt-rejecting dense membrane. When water is extracted into the draw solution, the diluted draw solution is, subsequently, sent to a regeneration device (e.g., RO or MD) to recover the purified water. The commonly used FO membrane has an RO-like or nanofiltration (NF)-like selective layer that has high rejection toward organic/inorganic compounds in the wastewater including ions. Normally two-phase flow around fiber bundles (for a hollow fiber module) or between vertical flat plates (for a flat sheet membrane module) by air scouring is used to control membrane fouling and module blocking.

Major Challenges for Large-Scale Applications

There are three major technical challenges that impede large-scale applications of FOMBRs. Firstly, an appropriate membrane is essential to improve the performance of the FOMBR. Commonly used FO membranes consist of a dense-selective layer supported by a porous substrate. The membrane should exhibit high water flux and high salt rejection and be able to limit feed-side fouling and internal concentration polarization (ICP), which is a unique phenomenon in the forward osmosis process, causing the reduction of the effective osmotic driving force. The strategy to overcome the problem is to design the support layer of the FO membrane as thin and porous as possible to reduce mass transfer resistance, and thus, less severe ICP is expected (Wang et al. 2010). Fouling is a common issue in a conventional MBR as the wastewater is a complex system containing microorganisms, extracellular polymeric substances (EPS), and soluble macro-/microorganics and inorganics. FOMBR, on the other hand, has an additional potential scaling issue caused by inorganic salts due to solute accumulation (Zhang et al. 2012).

Secondly, the bioprocess must be optimized to handle accumulated recalcitrant organics, nutrients, and elevated salt concentrations, as the FO membrane possesses a dense-selective layer with high retentions to the organic species and salts. The accumulation of organic matters improves the biological degradation which may enhance the removal of micropollutants. The salt accumulation, however, (i) could have adverse effects on biological treatment and cause microbial inhibition (Zhang et al. 2012; Nawaz et al. 2013); (ii) reduces the osmotic driving force available, resulting in the reduction of water flux; and (iii) increases the concentration of sparingly soluble salts, and spontaneous chemical precipitation may occur when the saturation limits are exceeded, leading to scaling on the FO membranes.

The third challenge relates to draw solute selection and regeneration. A proper draw solution is necessary to provide high osmotic pressure and low salt back diffusion (Cath et al. 2006). When the salts from the draw solution diffuse to

the feed tank, the driving force will be reduced, leading to flux decline and toxic effects on the microbial community. In addition, the draw solution must be able to be regenerated easily and economically for reuse (Cornelissen et al. 2008).

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Fossil Fuels Processing by Membrane Operations

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Control of anthropogenic emissions of greenhouse gases (GHG) is one of the most challenging environmental issues related to global climate change. The larger part of emissions are coming from fossil fuels. The Energy Information Administration (EIA) 2010 predicted a 49 % increase of

Fossil Fuels Processing by Membrane Operations, Table 1 Overview of global stationary CO₂ sources larger than 0.1 million tons (Mt) of CO₂/year

Process		Number of sources	Emissions (Mt CO ₂ /year)
Fossil fuels	Power	4,492	10,539
	Iron and steel industry	269	646
	Cement production	1,175	932
	Refineries	638	798
	Petrochemical industry	470	379
	Oil and gas processing	N/A	50
	Other sources	90	33
Biomass	Bioethanol and bioenergy	303	91
Total		7,887	13,468

(IPCC special report on CCS, working group III)

energy demands from 2007 to 2035 following more and more countries becoming industrialized. The International Energy Outlook 2010 reference case reported that world energy-related carbon dioxide (CO₂) emissions would increase from 29.7 billion metric tons in 2007 to 33.8 billion metric tons in 2020 and 42.4 billion metric tons in 2035 (IEO 2010). The emissions of the greenhouse gas CO₂ is produced in a variety of ways as shown in Table 1 (Hay and Firman 2002). Among them, fossil fuel power plants are responsible for roughly 40 % of total CO₂ emissions, and coal-fired power plants being the main contributor. Changing from fossil energy to alternative renewable energy would be ideal; however, we will still be dependent on fossil fuels for many years ahead both due to limitations of technology development and also increased growth. Hence, carbon capture and sequestration (CCS) is seen as an efficient way to mitigate the emission of CO₂ in order to fight against global warming. The key motivation for CCS is that we may continue to use fossil fuels without causing significant CO₂ emissions. Clearly coal-fired power plants need to be firstly tackled, especially by retrofitting capture to existing plants. Different techniques such as chemical and physical absorption, physical

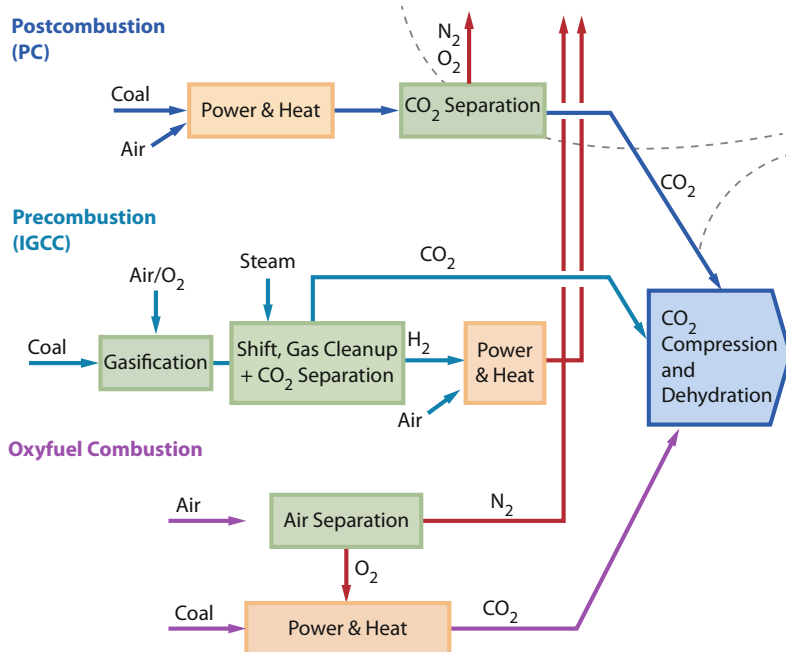
adsorption, cryogenics, and membrane separation may be used for CO₂ capture. Membranes are already an alternative and competitive technology for other selected gas separation processes such as natural gas sweetening, biogas upgrading, and hydrogen production during the last two or three decades. Alternative ways of using membranes for fossil fuel processing at power plants are illustrated in Fig. 1. Additionally, membranes are also being used for CO₂ removal from natural gas and upgrading of biogas.

Postcombustion: The membrane is then typically retrofitted to the plant as an end-of-pipe solution, and the main gas components are CO₂ and N₂. For a coal-fired power plant the content of CO₂ will be 10–15 %, while for a natural gas plant the CO₂ content may be as low as ~5 % unless there is an integrated solution. The flue gas will at this point have a temperature of around 70 °C and is at atmospheric pressure. These conditions are in general not very favorable for membrane separation as there is hardly any driving force, and much energy must be used in order to create sufficient partial pressure difference over the membrane. The recommended membrane solution in this case will be to use a membrane with very high flux and selectivity which can be achieved with a facilitated transport membrane having a fixed or mobile carrier to enhance the transport (Kim et al. 2004), or to use an innovative two-stage process solution where air is being used as sweep on the second stage and fed to the burner (Merkel et al. 2010). In both cases, energy demand is minimized by using only a fan on the feed side and pulling vacuum on the permeate side. The membrane material will be polymeric. Impurities in the flue gas stream (SO₂, NO_x, particles) may be a challenge for the membrane material.

Precombustion: When used in precombustion the membrane will be an integrated solution with the gas turbine and CO₂ may thus be removed at higher pressure. After the shift reaction H₂ and CO₂ will be in a mixture, with close to 40 mol% CO₂. The pressure will be in the range of 25–30 bar, and temperature around 300–350 °C unless there has been a sulfur removal unit up front of the membrane. The high temperature,

Fossil Fuels Processing by Membrane Operations,

Fig. 1 Alternative membrane processing at a power plant



pressure, and concentration are very favorable for Palladium membranes which can achieve extremely efficient separation of the two main components, allowing hydrogen to permeate (Jordal et al. 2004). An advantage is also that CO₂ is captured at high pressure, and less energy

will be needed for sequestration. The main challenge for this membrane solution is the module construction at this high temperature and also potential poisoning of the membrane.

Oxyfuel combustion: This solution is very elegant, using a membrane to separate out pure

oxygen. The air separating membrane is, however, still not fully developed. These membranes are suitable for advanced power generation requiring pure oxygen for combustion or gasification and are based on zirconia and perovskite where oxygen is transported through the material as O_2^- . The materials are stable at very high temperatures ($>500^\circ C$) but again module design is very challenging at these high operating temperatures.

Cross-References

- [Oxygen Transport Ceramic Membranes: Perovskite and Nonperovskite](#)

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Fouling

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Synonyms

[Fouling in membranes](#); [Membrane fouling](#)

An intrinsic phenomenon of all membrane separation processes is the decline of the flux through the membrane as a function of time, due to concentration polarization effects and the formation of cake or gel layers by feed solution constituents retained by the membrane. Equally devastating

for the performance of a process is membrane fouling. Membrane fouling is a general term. It may be the result of concentration polarization; it may also be the consequence of adsorption of feed solution constituents at the membrane surface and especially in microfiltration also within the membrane structure. The control of concentration polarization and membrane fouling is a major engineering aspect in the design of membrane separation processes and equipment (Brian 1966; Blatt et al. 1970; Jonsson and Boesen 1984; Bian et al. 2000; Hoek and Elimelech 2003; Cornelissen et al. 2004).

Concentration polarization effects will occur in all membrane separation processes. Its consequences, however, are especially severe in pressure-driven membrane processes. When in a mass separation procedure a molecular mixture is brought to a membrane surface, some components will permeate the membrane under a given driving force, while others are retained. This leads to an accumulation of retained material and to a depletion of the permeating components in the boundary layers adjacent to the membrane surface. This phenomenon is referred to as concentration polarization. The causes and consequences of concentration polarization may be rather different in different membrane processes. Often the adverse effects of concentration polarization are intensified by an adsorption of certain feed mixture constituents at the membrane surface. This phenomenon is referred to as membrane fouling.

Concentration polarization can be minimized by hydrodynamic means such as the feed flow velocity and the membrane module design. The control of membrane fouling, however, is more difficult. The transition between concentration polarization and fouling can be expressed by the concept of “critical flux.” This concept was introduced in the 1990s (Field et al. 1995; Howell 1995; Bacchin 2004), and it is the flux value below which a decline of flux with time does not occur, above it fouling is observed. Critical flux values depend on numerous parameters, such as properties of solutions to be treated (particle size, concentration, ionic strength, pH), surface interactions (zeta potential, surface tension), and hydrodynamic conditions (axial velocity)

(Bromley et al. 2002; Chen 1998; Ingmar et al. 1999; Belfort et al. 1994).

When operating below the critical flux, it is possible to observe a linear correlation between flux and transmembrane pressure. Above it, further increase in transmembrane pressures lead to additional layer deposit on the membrane surface, until a point where the deposit fully compensates the increase in pressure drop. At this stage the limiting flux is reached, which represents the maximum stationary permeation flux. After operating above the critical flux value, decreasing the transmembrane pressure will not lead to the previous flux behavior.

However, experimental evidences show that, although operating at subcritical flux, gradual fouling develops in membrane materials, and it proves to be hydraulically irreversible after a long period experimentation (Ognier et al. 2004).

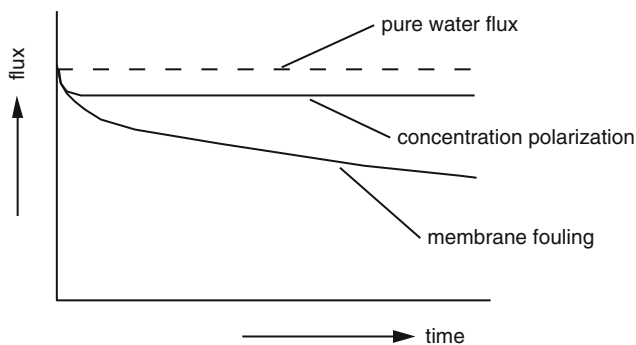
The formation of a gel or cake layer is one cause for membrane fouling. Gel or cake layer formation may be caused by a variety of materials including inorganic precipitates such as CaSO_4 , Fe(OH) , and other metal hydroxides; organic materials such as proteins, humic acids, and other macromolecular materials; and biological components such as microorganisms and products of their metabolism (biofouling). Membrane fouling may also occur without concentration polarization, i.e., a direct transport to the membrane surface. The attachment of the substances to the membrane surface may be caused by adsorption due to hydrophobic interactions, van der Waals force attractions, or electrostatic forces. The fouling layer itself may be rather porous and thus permeable for aqueous solutions as some

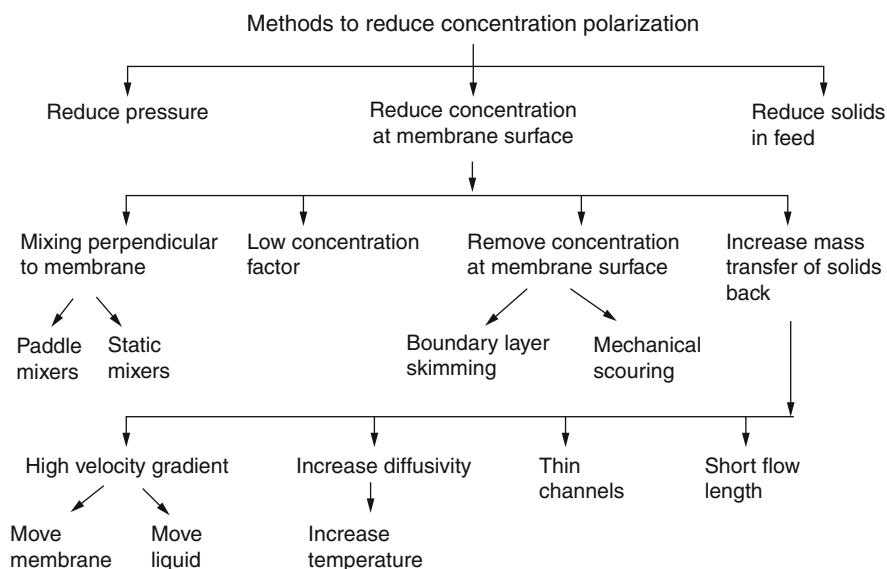
inorganic precipitants or highly impermeable as some films of mineral oils or hydrophobic surfactants. The fouling mechanism depends also on the membrane process. In electrodialysis fouling is caused mainly by the precipitation of polyelectrolytes or sparingly soluble salts such as CaSO_4 or CaCO_3 . Membrane fouling in electrodialysis affects mainly the anion-exchange membranes because most of the colloidal and macromolecular polyelectrolytes present in natural waters such as humic acids or proteins are negatively charged. In ultra- and microfiltration of biological solutions, but also in reverse osmosis of sea water, biological fouling is a severe problem affecting the economics of the processes. In biomedical applications protein adsorption and protein denaturation at the membrane surface is often impairing the performance of the membranes. In membrane distillation, adsorption of molecules can change surface energy and hydrophobic properties.

The difference between concentration polarization and membrane fouling or scaling is illustrated schematically in Fig. 1.

Concentration polarization is a reversible process based on diffusion and takes place over a few seconds; it can be described adequately by a simple mathematical model and easily be controlled by the proper process design. Fouling is generally irreversible and the flux decline takes place over many minutes, hours, or even days. A constant flux is generally not reached at all. Membrane fouling is more difficult to describe and to control by experimental means. Membrane fouling is determined by a variety of different parameters including the feed solution constituents and their

Fouling, Fig. 1 Schematic diagram illustrating the difference between the flux decline due to concentration polarization and due to membrane fouling





Fouling, Fig. 2 Methods to reduce concentration polarization

concentration, membrane material, and the fluid dynamic system design. Membrane fouling can be caused by simple precipitation of insoluble materials or reversible and irreversible adsorption of components at the membrane surface and within the membrane pores.

The means of preventing or at least controlling membrane fouling effects are as heterogeneous as the different material and mechanisms causing the fouling (Ridgway et al. 1983; Nilson 1998). The main procedures to avoid or control concentration polarization and fouling involve:

- Pretreatment of the feed solution
- Membrane surface modifications
- Hydrodynamic optimization of the membrane module
- Membrane cleaning with the proper chemical agents

A list of various methods to reduce concentration polarization is reported in Fig. 2.

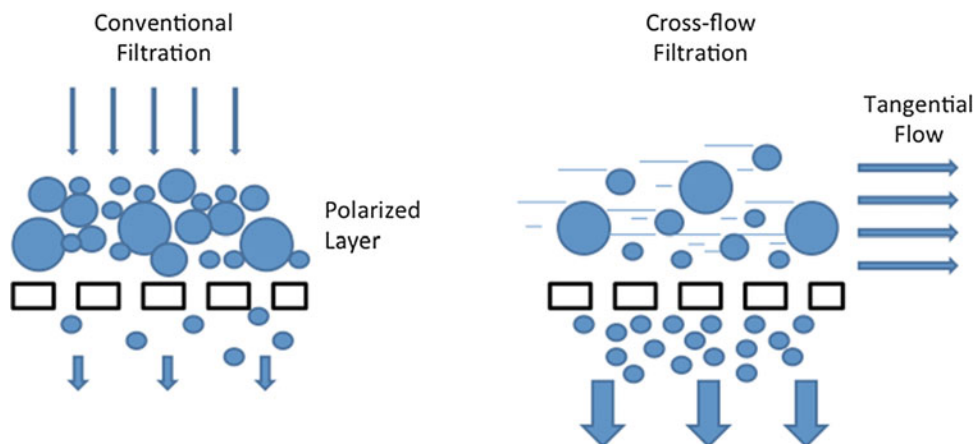
A pretreatment of the feed solution may include chemical precipitation, prefiltration, pH adjustment, chlorination, or carbon adsorption. In some membrane module, design concepts as, for instance, in hollow fiber modules, the

elimination of all particulate materials is of great importance for the proper function of the membrane.

Membrane surface modifications include the introduction of hydrophilic moieties or charged groups in the membrane surface by chemical means or plasma deposition.

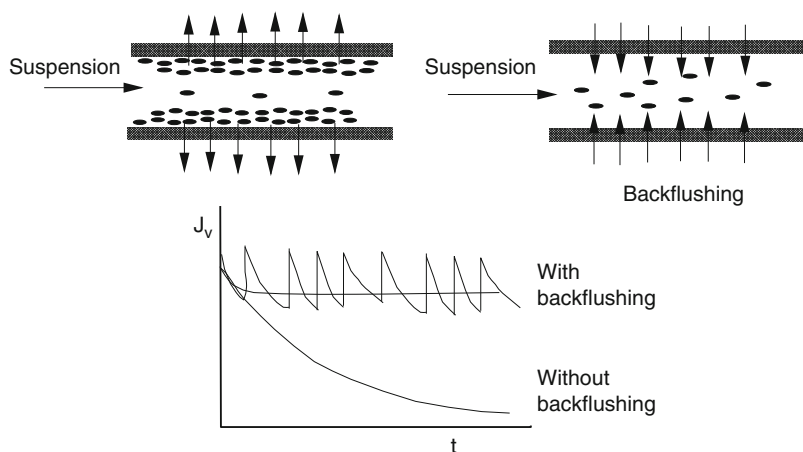
Increasing the shear rate imposed by the feed solution on the membrane surface will in many cases reduce the membrane fouling. High feed flow velocities and the proper module design are efficient tools in controlling membrane fouling (Fig. 3).

When in spite of an adequate membrane and module design the membrane flux is decreasing with operation time to an unacceptable low value, it is necessary to clean the membrane to restore the flux in part or completely. Typical cleaning agents are acids and bases, such as HNO_3 and NaOH , complexing agents, enzymes, and detergents. Another very effective method to minimize the effects of membrane fouling in microfiltration is backflushing (Fig. 4). In backflushing, the applied pressure is reversed and the permeate is pushed through the membrane, lifting off fouling material that had been precipitated on the feed side membrane surface and washing it out of the filtration



Fouling, Fig. 3 Effect of axial velocity on concentration polarization

Fouling, Fig. 4 Backflushing method to reduce fouling



device. Backflushing is done in certain time intervals for a couple of seconds.

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lifetime of metastable amorphous phase is strongly governed by the exact solution environment, with the presence of other additive molecules and ions, pH, ionic strength, and temperature affecting the lifetimes. The transformation of amorphous to crystalline hydroxyapatite is described by a first-order rate law and is only a function of pH of the mediating solution at constant temperature. Crystalline calcium phosphate apatite is less soluble in neutral and alkaline conditions and preferentially dissolves in acidic pH.

A calcium phosphate stability index based on the phosphate concentration, temperature, and pH (Kubo et al. 1979) helps to predict the threshold level of scaling (Filmtec 1995).

$$SI = pH_a - pH_c$$

where pH_a is the actual pH of a feed water and pH_c is the critical pH calculated as below:

$$pH_c = \frac{11.755 - \log(CaH) - \log(PO_4) - 2\log t}{0.65}$$

where CaH is the calcium hardness as ppm $CaCO_3$, PO_4 is the phosphate concentration as ppm PO_4 , and t is the temperature in $^{\circ}C$.

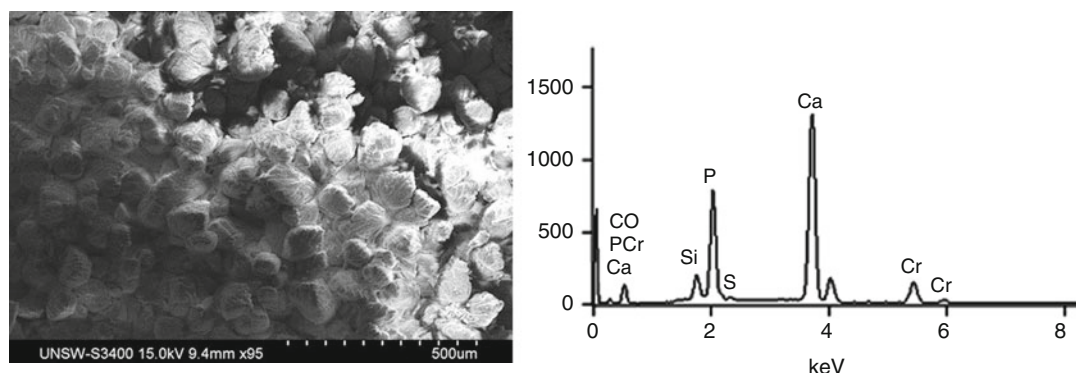
Phosphate can form a variety of polymeric ions and therefore many forms of phosphate salts are possible to be formed as a scale; however, the majority of calcium phosphate deposits are reported to be amorphous in nature (Chesters 2009). During membrane autopsy studies, calcium phosphate scaling was mostly observed as coprecipitated along with other organic and/or inorganic constituents (Fig. 1).

The state at which the calcium phosphate enters the RO system is expected to govern the nature of the deposit forming on the membrane surface (Ning and Troyer 2007). After pretreatment, if calcium phosphate is in its dissolved form, i.e., calcium and orthophosphate ions, then crystallization of calcium phosphate is more likely to occur on the membrane surface. On the other hand, if calcium phosphate is in its colloidal form, colloidal deposits are more likely to form on the membrane surface, instead of

Fouling due to Calcium Phosphate

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Calcium phosphate scaling occurrence is largely reported in reverse osmosis (RO) applications for the reclamation of wastewater (Chesters 2009; Greenberg et al. 2005; Zach-Maor et al. 2008). In municipal wastewater, phosphate levels typically range between 3 and 20 ppm, presenting a major operational challenge for systems designed to operate at high product recoveries. The crystalline forms of calcium phosphate are hydroxyapatite and fluorapatite, which are calcium orthophosphates with varying amounts of OH-, Cl-, and F-groups. Formation of hydroxyapatite occurs through autocatalytic solution-mediated transformation of highly unstable amorphous calcium phosphate, hydrolyzing rapidly to more stable hydroxyapatite microcrystals in water. The



Fouling due to Calcium Phosphate, Fig. 1 SEM-EDS images showing calcium phosphate scaling on RO membrane operated with paper mill effluent (Picture provided by Dr Alice Antony, The University of New South Wales, Australia)

crystallization. In these cases, antiscalants will be ineffective at their typical dosage levels, and therefore anticoagulants or dispersants should be added.

Unlike other scales, mitigating calcium phosphate scales through antiscalant addition is reported to be difficult (Greenberg et al. 2005; Ning and Troyer 2007). However, the risk of calcium phosphate precipitation can be minimized by maintaining the feed water below pH at 6.4 (Zach-Maor et al. 2008). Use of appropriate dispersants is an effective control measure when calcium phosphate is in the form of nanoparticles in the feed. The risk of calcium phosphate scaling can also be managed to a certain extent by reducing the concentration of orthophosphate, calcium, aluminum, iron, and fluoride at the pretreatment stage.

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Further Reading

Antony A, Low JH, Gray S, Childress AE, Le-Clech P, Leslie G (2011) Scale formation and control in high pressure membrane water treatment systems: a review. *J Membr Sci* 383:1–16

Fouling in Membranes

► Fouling

Fouling Index

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Synonyms

Combined Fouling Index (CFI); Membrane Fouling Index; Modified Fouling Index (MFI); Silt Fouling Index (SFI)

Membrane fouling is an inevitable phenomenon in membrane processes and reduces the efficiency and the economic viability of the membrane processes. All the fouling stages such as pore blocking and cake layer not only decrease the permeate flux during a membrane process but they could influence negatively the permeate quality. Understanding the membrane fouling means that it is possible to develop a method to measure and predict the fouling potential with respect to a membrane. There is a pressing need for a reliable method able to do that.

Simple membrane experiments such as Silt Density Index (SDI) and Modified Fouling Index (MFI) are fouling index methods used to evaluate the particulate fouling potential of a feed water on reverse osmosis (RO) and nanofiltration (NF) membrane process (Salinas-Rodriguez SG et al. 2015). The utilization of fouling indices enables to determine, e.g., the pretreatment requirements without conducting a pilot study which needs considerable time and expenses. Although these indices are the standardized parameters and widely used in engineering practices, they are considered to be unsatisfactory indicators that often fail to reflect the true fouling strength of the feed water.

SDI and MFI are performed using a membrane with 0.45 μm pores. The SDI test, defined by a standard method instructed in ASTM-D4189-07 (2014), is a dead-end filtration conducted on the feed at 207 psi through a 47 mm diameter microfiltration membrane with 0.45 μm pores. The rate of plugging is measured and expressed as % flux decline per minute. Fouling index by SDI is obtained by Eq. 1:

$$\text{SDI} = \frac{[1 - (t_i/t_f)]}{t} \cdot 100 \quad (1)$$

In Eq. 1, t_i is the initial time interval to collect 500 ml of permeate, and t_f is the final time interval to collect the same volume of permeate after a time interval t of 5, 10, and/or 15 min.

The limitations of the SDI test are well documented (Alhadidi et al. 2011; Rachman et al. 2013; Nahrstedt et al. 2008), and include: no correction for test water temperature; the result is

heavily dependent on the test membrane permeability; not applicable for testing high fouling feed water, e.g., raw water (ASTM recommends that turbidity should be <1 NTU); not applicable for testing UF permeate, which is increasingly being used in desalination pretreatment; no linear relation with colloidal/suspended matter; fouling potential of particles smaller than 0.45 μm is not measured; and it is not based on any filtration mechanism.

To overcome these deficiencies, the Modified Fouling Index using the same 0.45 μm membrane filters ($\text{MFI}_{0.45}$) was developed. The $\text{MFI}_{0.45}$ can achieve the linear relationship between concentration and flux decline, but still cannot accurately predict flux decline. Boerlage et al. (2002) confirmed that this is due to the fact that in RO, fouling is caused by smaller colloids that are not retained by the microfiltration membranes used in the MFI. Seeing the above complexities of fouling mechanisms, this is not unexpected. The $\text{MFI}_{0.45}$ test is similar to the SDI test (Schippers and Verdouw 1980), but the volume is recorded every 20 s for 20 min. It takes into account that initially pore blocking occurs, followed by cake/gel filtration, and finally cake/gel blocking and/or enhanced compression occurs. The cake filtration can be identified by plotting t/V versus V , where t is the time and V is the volume. The slope in this region is the fouling index. The obtained $\text{MFI}_{0.45}$ value is corrected for temperature and pressure and shows a linear relation with colloidal/suspended matter concentration. *MFI* is derived in Eq. 2, and it is defined as the slope of an inverse flow rate ($1/Q$) versus cumulative volume (V) curve:

$$\frac{1}{Q} = a + \text{MFI} \cdot V \quad (2)$$

Predicting the rate of fouling in RO systems based on the $\text{MFI}_{0.45}$ is possible, assuming that cake/gel filtration is the dominant mechanism. However, the predicted rate of fouling turns out to be very low for MFI of 1 s/L² (equivalent to SDI_{15} 1–3). A pressure increase of 1 bar is predicted to occur in more than 100 years with RO feed water with an $\text{MFI} = 1 \text{ s/L}^2$.

Both $\text{MFI}_{0.45}$ and SDI underestimate the fouling observed in practice.

As the SDI and the $\text{MFI}_{0.45}$ do not include smaller colloid sizes, a new index using an ultrafiltration (UF) membrane has been developed. Boerlage et al. tested this MFI-UF as a function of molecular weight cutoff (MWCO, 1–100 kDa) of the UF membranes and obtained values ranging from 2000 to 13,000 s/L2 (as compared to $\text{MFI}_{0.45}$ values of 1–5 s/L2). Higher values were linked to the retention of smaller colloids as well as cake filtration of the retained particles, although a correlation with the MWCO was not apparent. While other membrane characteristics may be partly responsible for those varied results, it is also important to note that fouling at such MWCOs is complex and cannot be solely attributed to particulates. A 13 kDa membrane was established to be the best membrane for such tests.

Boerlage et al. used a 13 kDa UF membrane (estimated pore dimension 9 nm) to measure fouling potential and effectiveness of pretreatment and compare the results with the SDI and the $\text{MFI}_{0.45}$. MFI-UF can be operated in constant flow or pressure mode. The MFI-UF values were in fact 400–1400 times higher than the $\text{MFI}_{0.45}$ due to the smaller particles captured. The MFI-UF can also be used to determine the effectiveness of pretreatment with regard to reduction of fouling potential. Roorda and van der Graaf (2001) used the MFI-UF to determine the fouling potential of UF membranes and confirmed the dependence on membrane type. As a general evaluation, Reiss and Taylor compared three parameters used to investigate fouling: the Silt Density Index (SDI), the Modified Fouling Index (MFI), and the linear correlation of the water mass transfer coefficient (MTC). Three different NF pilot systems were used with different pretreatments including activated carbon and MF. No correlation between the different parameters was obtained, indicating that the filtration laws on which the models are based might not be valid for NF. Hence, these parameters need to be used with caution.

SDI and MFI seem to be difficult if there is more than one type of fouling mechanisms. Another approach to estimate fouling potential

due to various fouling mechanisms is attempted by combining MFI values measured using multiple test membranes. This method, which is designated as the Combined Fouling Index (CFI), allows considering the contribution of particles, hydrophobic matters, colloids, and organics to RO/NF fouling at the same time. J.-S. Choi et al. (2009) used three different membranes: a hydrophilic microfiltration membrane, a hydrophobic microfiltration membrane, and a hydrophobic ultrafiltration membrane in order to study the efficiency of different pretreatments. The Combined Fouling Index value was obtained using Eq. 3:

$$\text{CFI} = \omega_1 M_1 + \omega_2 M_2 + \omega_3 M_3 + \omega_4 \quad (3)$$

where M_1 , M_2 , and M_3 are the MFI values of the three membranes and ω_1 , ω_2 , ω_3 , and ω_4 are weighting factors depending on the characteristics of RO/NF membrane because they are closely related to fouling mechanisms. The weighting factors were calculated from the flux decline rate of each membrane.

CFI values are in good agreement with nanofiltration flux decline because with this test is possible considering the impact of different foulants.

In addition, it is also possible to use more than three test membranes to obtain more information on the characteristics of feed water.

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Fouling Release

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Fouling release is one of the general strategies to achieve desired non-fouling surfaces. Any surface immersed in a specific aqueous system (wastewater, seawater, tap water, etc.) is subjected to the undesirable settlement and nonspecific adsorption of biomolecules (e.g., protein and polysaccharide), natural organic matter, hydrocarbon, and microorganism (e.g., bacteria, algae, and mollusks), known as fouling. Non-fouling surfaces to resist different foulants are vital in a wide range of applications including chemical separation and purification, drug delivery systems, biomaterials, biosensors, and marine coatings. The concept of fouling release initially comes from marine non-biocidal coating. Fouling release refers to the feature that the attached and

adhering foulants are more easily removed from the depositing surfaces at low hydrodynamic shear forces due to the weakened interfacial bond between the synthetic surface and different foulants, promoting adhesive failure. The release ability of foulants is proportional to the surface energy and modulus (gE)^{1/2} (Brady and Singer 2000). The lower the surface energy and modulus, the stronger reduction of the enthalpy of adsorption and the higher fouling release potential of the surface. Surface with compositional heterogeneous hydrophobic/hydrophilic domains can also reduce interactions with the bioadhesives. In the design of surfaces to eliminate the adhesion of various foulants, polysiloxane- and fluorinated polymer-based surfaces are usually hydrophobic and most effective in reducing adhesion. The major advantage of polysiloxane-based surfaces is the synergy between low surface energy (to minimize the work of adhesion) and low elastic modulus. The major advantage of fluorinated polymer-based surfaces lies in hydrophobicity and oleophobicity with low surface energy.

Marine non-fouling coatings provide a source of inspiration for fouling release membrane. Membranes with fouling release property are essential for preventing fouling growth on the surfaces whose antifouling performance relies on the low adhesion strength and easy release of foulants on such a membrane. In recent years, surface modification of membranes using low surface energy materials to enhance fouling release ability is under active studying microfiltration, ultrafiltration, nanofiltration, reverse osmosis, etc. The surface energy and heterogeneities are introduced in the elucidation of membrane fouling release mechanism during membrane filtration. The lower surface energy and larger chemical heterogeneity correspond to a lower driving force for the adsorption of the foulants, thereby resulting in effective fouling release ability. Surfaces which fulfill these requirements are often derived from polysiloxane- and fluorine-based polymers. In situ forced surface segregation of amphiphilic copolymers and grafting low surface energy molecules or monomers to already formed membranes are popular methods to fabricated

fouling release membrane. Membranes with low surface energy chains (such as PDMS, poly(ethylene glycol)-fluoropolymers, perfluoroalkyl polymers, perfluoropolyether polymers, and fluorine-containing block) showed a high release rate. The release rates of PDMS and perfluoroalkane polymer-functionalized membranes are about five times higher than those of hydrophilic surface as a result of the low interaction between the low surface energy surfaces and protein (Thérien-Aubin et al. 2011). There is a growing body of evidence that amphiphilic or chemically heterogeneity membrane surfaces can present both low surface energy and high hydration energy microdomains and show promising performance against a wide range of foulants. Membrane prepared from amphiphilic copolymers with hydrophilic segments and fluorine-containing segments via nonsolvent-induced phase separation (NIPS) process through forced surface segregation showed enhanced oil, protein, and bacteria release ability (Chen et al. 2011). The low surface energy microdomains on the membrane surface minimize the intermolecular forces of interactions (polar or and hydrogen-bonding interactions) between the foulants and the membrane surface, remarkably reducing the flux decline and reducing energy consumption during the dynamic filtration process.

In the application of antifouling membranes for water treatment and biomedical application, fouling release membranes offer an interesting alternative to environmentally friendly strategies to facilitate foulants removal, such as hydrocarbon substances, biomolecules, and microorganisms.

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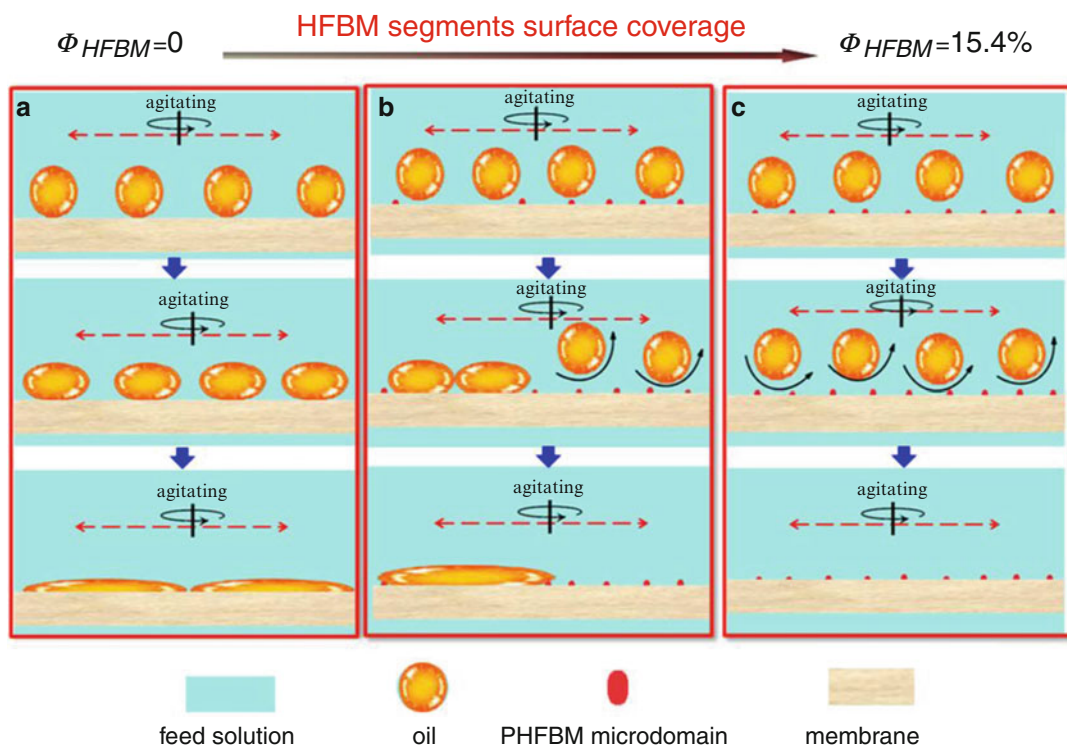
Fouling Release Membranes

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Fouling release membrane is a novel kind of membrane that has the chemical structure and main feature of nonpolar low surface energy microdomains and hydrophilic domains, inhibiting the nonspecific adsorption of a variety of foulants. The low surface energy microdomains on the membrane surface, which can be constructed with silicone- and fluorine-based polymers, are used to minimize the intermolecular forces of interactions (polar and/or hydrogen-bonding interactions) between the foulants and the membrane surface. The hydrophilic domains are used to bind water molecules and generate hydration layer similar with widely popular hydrophilic modification methods. Considering that foulants tend to adsorb on traditional hydrophobic membrane surfaces driving by the decrease of the Gibbs free energy of the system, the surface energy of membranes is regarded as one of the most relevant physicochemical parameters influencing free energy of the adsorption process. The reduction of the surface energy causes a strong reduction of the enthalpy of adsorption which describes the strength of interaction between the protein and the surface and thus strongly decreases the driving force for the foulants to adsorb to the surface (Worz et al. 2012). Due to the presence of nonpolar low surface energy microdomains on the membrane surface, foulants in the feed solution can easily release from the membrane surface and diffuse back to the bulk feed solution during the dynamic membrane filtration process. Inspired by marine fouling release materials, this kind of membrane is



Fouling Release Membranes, Fig. 1 Tentative illustration of the flux decline resistant mechanism of membranes (Chen et al. 2011b)

initially designed to detach the foulants from the surface at low hydrodynamic shear force, and now it is applied to achieve low permeation flux decline and high permeation flux recovery simultaneously during the membrane filtration process.

To construct fouling release membrane surface, majority of the existing researches have been carried out to reduce the surface free energy through fluorine-based polymers. In situ forced surface segregation and post-surface grafting are the two general surface modification methods being explored to introduce low surface energy microdomains onto the membrane surface. In the process of the forced surface segregation, amphiphilic copolymers with hydrophilic segments and fluorine-containing segments are used as additives or polymer membrane materials as that usually applied in surface segregation approach. Considering that fluorine-containing segments

are not able to spontaneously segregate onto the polymer-water interface due to the unfavorable thermodynamics, the forced surface segregation coupled with nonsolvent-induced phase separation process is proposed for achieving membrane surfaces with fluorine-containing microdomains. In the immersion-precipitation step, hydrophilic segments of the copolymers segregate to the polymer-water interface freely and drag the fluorine-containing hydrophobic segments to enrich on membrane surfaces. Both the composition of hydrophilic and hydrophobic segments and the volatility of casting solvent can affect the surface segregation behavior and the fouling release ability of membrane surfaces (Chen et al. 2011a, b). The membrane materials used in the post-surface grafting method must be rich of reactive groups. Surface grafting by chemical reaction is a facile method for introducing low surface energy microdomains onto hydrophilic

membrane surfaces. Low surface energy perfluoroalkyl or even polysiloxyl molecules with active groups are used as modifiers to improve the fouling release ability of membrane (Thérien-Aubin et al. 2011; Zhao et al. 2012).

Although hydrophilic surface modification can significantly enhance the antifouling property of the membrane, it, unfortunately, often results in a drastic flux decline during the separation and purification process. Fouling release membrane is an alternative to traditional hydrophilic membrane which leads to lower permeation flux decline. Figure 1 reports a tentative flux decline resistant mechanism of fouling release membrane. The random presence of nonpolar low surface energy (typically fluorinated) microdomains on the hydrophilic membrane surface creates a surface with chemical heterogeneity that is vital to constructing a truly fouling release membrane surface. At moderate shear rate along membrane surface, nonpolar low surface energy microdomains prevent the coalescence, migration, and spreading of the hydrophobic oil droplets or limit the accumulation/coalescence of polar biofoulants, thus endowing the membrane surface with outstanding fouling release potential without inducing a flux decline.

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Fractional Free Volume (FFV)

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Fractional free volume (FFV) is an empirical dimensionless parameter that characterizes free volume in polymers. FFV can be defined as the ratio V_f/V_{sp} , where V_f (cm³/g) is the free volume and V_{sp} (cm³/g) is the specific volume of the polymer, the latter parameter being the reciprocal density ρ . The value of V_f can be calculated using Bondi (1968) formula $V_f = V_{sp} - V_{oc}$, where V_{oc} is the occupied volume, and it can be estimated as $V_{oc} = 1.3 V_w$, where V_w is van der Waals volume of the repeat unit of the polymer. Such an estimate gives the FFV values of most polymers in the range of 10–25 %. However there are examples when FFV is as large as 35 % (polytrimethylsilyl propyne). In spite of its wide usefulness, such definition of FFV has many disadvantages and is being often criticized. In the case of glassy polymers, the density may depend on prior history of the sample and, to some extent, on the method of determination. The coefficient 1.3 in calculating V_{oc} is estimated from packing density of molecular crystals at 0 K and cannot adequately describe polymers at room temperature. In addition, calculation of V_w of a repeat unit as the sum of the increments of van der Waals volumes of atoms that form this repeat unit can lead to some inaccuracies. Since this approach poorly takes into account the dead volume which depends on conformations of the chain and is different for different gases, quantum chemical corrections are desirable. More reliable results were reported by Ronova et al. (2003). So FFV found in this way can be considered as a semi-quantitative parameter suitable for comparison of series of polymers. Park and Paul (1997) assumed that FFV can be considered not as a universal property of polymers. Gases with

different molecular dimensions can “feel” different parts of the size distribution of free volume. So an empirical method for calculation of occupied volume specific for each gas was proposed. This group contribution method allows better predictions of the permeability coefficients based on modified FFV.

Positron annihilation lifetime spectroscopy (PALS) also allows an estimation of fractional free volume as $FFV = Nv_f$, where N is hole number density (concentration of holes) and v_f is the mean volume of the spherical hole with the radius R in the polymer or $v_f = 4/3 (\pi R^3)$. The FFV values found in this manner are usually smaller than FFV estimated via Bondi by a factor 3–4. It is explained by the fact that a big fraction of size distribution of free volume in polymers consists of holes with the radii inaccessible to o-positronium having the size of 1.06 Å. This is confirmed by the calculations using molecular dynamics method (Hofmann et al. 2002): extrapolation of FFV to the zero radius of probe results in FFV values much greater than those found via PALS.

Cross-References

- [Dynamic Free Volume](#)
- [Free Volume Distribution](#)
- [Free Volume Element](#)

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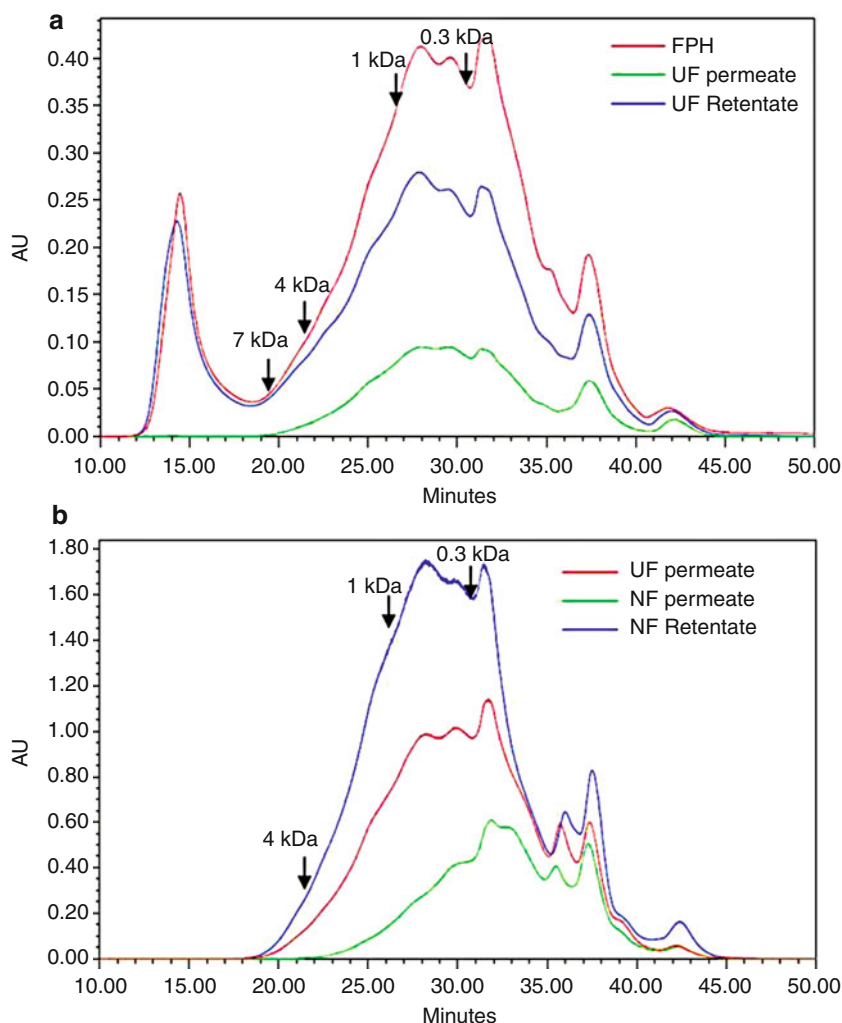
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Fractionation of Fish Protein Hydrolysates

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Each year the processing industry of marine species generates large amounts of solid by-products such as filleting wastes, heads, etc. which are usually converted to fish meal and oil for feed. However, these by-products often contain high concentrations of proteins that can be transformed into peptides through enzymatic hydrolysis. Fish protein hydrolysates (FPH) possess good nutritional properties and biological activities such as antioxidative, anticarcinogenic, immunological activities, etc. (Chalamaiah et al. 2012). They can thus represent marketable and value-added products to be used as food and feed. Although biological properties of peptides are related to various characteristics, molecular weight (MW), amino acid sequence, hydrophobicity, charge, and acidobasic character, the MW seems to be one of the most important ones. In particular peptides with MW between 1 and 4 kDa have been identified as the most bioactive ones (Hsu 2010). The pressure-driven membrane processes thus appear to be good candidates to fractionate and concentrate FPHs in view to produce peptide fractions with high specific activity. Firstly peptides can be separated from nonhydrolysed proteins owing to UF with high molecular weight cutoff (MWCO) membranes (~20 kDa). Then peptide hydrolysates can be fractionated according to their size with UF membranes of intermediate MWCO (4–8 kDa); the recovery yields are improved if UF is combined with diafiltration. Finally the concentration of selected fractions can be carried out with nanofiltration (NF) membranes of low MWCO (200–300 Da) (Chabeaud et al. 2009; Vandanjon et al. 2009). Figure 1 shows the molecular weight distribution of different peptide fractions obtained after UF/NF fractionation of a tuna dark muscle hydrolysate.



Fractionation of Fish Protein Hydrolysates, Fig. 1 Molecular weight distribution of peptides obtained by enzymatic hydrolysis of tuna dark muscle – (a) Comparison of permeate and retentate obtained by UF combined with diafiltration (8 kDa ceramic membrane, (Inside CéRAM™, Tami Industries)) with the raw fish protein

hydrolysate (FPH) (feed of the UF step) – (b) Comparison of permeate and retentate obtained by NF (NP010, Microdyn Nadir) with the UF permeate (feed of the NF step) (Superdex-peptide HR 10/300 – Eluant: Water/TFA/ACN: 70/0.1/30)

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Fractionation of Milk by Membrane Operations

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Milk is a complex colloidal suspension containing many classes of different size components (salts, soluble proteins, casein micelles, fat globules, microorganisms, etc. (see Table 1)) which can be well separated from others according to their size or charge, thanks to membrane techniques (Brans et al. 2004; Pouliot 2008; Gésan-Guiziou 2010).

Since the 1980s, ultrafiltration (UF) has been widely used in dairy industries in order to concentrate the protein fraction of milk without any denaturation. This operation is generally carried out on spiral wound polymer membranes or to a lesser extent on tubular ceramic membranes with molecular weight cutoff (MWCO) 10–50 kDa and at a transmembrane pressure of 200–400 kPa. According to the concentration level, different types of concentrate can be distinguished. UF of skimmed milk with low volume reduction factors (VRF up to 1.7 (the ratio between either the

volumes of feed and retentate in discontinuous mode or flow rates of feed and retentate in continuous mode)) leads to the protein standardization of both drinking and cheese milks. The use of such milks permits a better process control of continuous cheese-making processes and leads to a constant quality of products throughout the year. The use of intermediate-concentrated retentates ($1.7 < \text{VRF} < 5$) and high-concentrated retentates (VRF 5–7) permits the continuous production of numerous cheese varieties (fresh unripened cheeses, soft and semihard cheeses) with high yield and very little whey drainage. All these cheese-making processes are derived from the famous worldwide process known as MMV process after the investigators Maubois, Mocquot, and Vassal (Gésan-Guiziou 2010).

Microfiltration (MF) is an alternative to centrifugation for the removal of bacteria and spores from skimmed milk in order to extend its shelf life without applying a time-temperature treatment. MF is thus carried out with multichannel ceramic membranes with a pore diameter of 1.4 μm at high tangential velocity ($6\text{--}9 \text{ m s}^{-1}$) and low transmembrane pressure (TMP) (50 kPa). In order to limit the fouling phenomena, a uniform TMP is applied all along the membrane, thanks to the circulation of the permeate cocurrent of the retentate (Bactocatch system[®], AlphaLaval; Invesys[®] APV) or thanks to the use of ceramic membranes with linear hydraulic-resistance gradient (GP Membralox[®] membrane Pall-Exekia; Isoflux[®] membranes Tami-Industries). MF of skimmed milk on a 0.2 μm ceramic membrane permits the concentration of casein micelles. One hundred percent of the caseins are recovered in the retentate without any denaturation, while the permeate which is sterile and free of phage particles presents a composition close to that of whey. It can be used to prepare whey protein concentrate (WPC) and isolate (WPI). Finally MF can be also used for the separation of milk fat into small ($< 3 \mu\text{m}$) and large ($> 5 \mu\text{m}$) globules. This operation is achieved with ceramic membranes with nominal pore size higher than 2 μm . The permeate which is enriched in small globule fraction leads to the production of cheeses with smoother and finer texture.

Fractionation of Milk by Membrane Operations, Table 1 Approximate composition of milk

Components	Concentration (g L ⁻¹)	Size (μm) or molecular weight (Da)
Water	870–875	
Fat	34–44	0.15–15 μm
Lactose	48–50	342 Da
Proteins	32–35	
Caseins (micelles)	25–28	50–500 μm
Soluble proteins	5–7	14.2–150 kDa
Ashes (mineral and salts)	8–9	

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Fractionation of Whey by Membrane Operations

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Whey is a coproduct of cheese-making and casein manufacture in the dairy industry; it is the liquid drained from the curd obtained after addition of rennet (chymosin) or mineral/organic, or the permeate obtained during skimmed milk microfiltration (MF) in view of casein concentration. Whey contains many classes of different-size components (salts, lactose, soluble proteins (mainly β -lactoglobulin and α -lactalbumin), residual casein, microorganisms, etc. (see Table 1)), but its composition depends on the cheese-making process. The addition of enzyme or rennet milk leads to sweet whey (pH 6.2–6.4), whereas acid whey (pH 4.6–5) is obtained after acidic coagulation of milk. Considered as waste for years, whey is now widely used as food ingredients in many goods and infant and dietetic foods. Owing to chromatographic, electrodialytic, and membrane techniques which permit whey fractionation, it is possible to prepare valuable proteins and peptides with high nutritional qualities (high biological value (BV), amino acid profile, etc.), interesting physical properties (gelling,

Fractionation of Whey by Membrane Operations, Table 1 Approximate composition of sweet and acid whey

Components	Sweet whey (%)	Acid whey (%)
Water	93–94	94–95
Lactose	4.5–5	3.8–4.3
Lactic acid	Traces	Up to 0.8
Fat	Traces	Traces
Total proteins	0.8–1.0	0.8–1.0
Soluble proteins	0.6–0.65	0.6–0.65
Ashes (mineral and salts)	0.5–0.7	0.5–0.7

foaming, water binding, etc.), and physiological functionalities.

Whey protein concentrates (WPC) containing 35–85 % protein are prepared by ultrafiltration (UF) with 10–20 kDa molecular weight cutoff (MWCO) membranes. According to the concentration level, different types of concentrate can be distinguished. For 35 % WPC, the volume reduction factor (VRF) – the ratio between either the volumes of feed and retentate in discontinuous mode, or flow rates of feed and retentate in continuous mode – is about 4–7, whereas VRF of 13–50 are required to prepare 50–60 % WPC. 75–85 % WPC are obtained owing UF (VRF 30–35) combined with diafiltration in order to remove minerals and lactose. Whey protein isolates (WPI) containing more than 90 % of proteins are generally produced from the microfiltration permeate of skimmed milk using ion-exchange chromatography (IEC).

Reverse osmosis (RO) permits the concentration of whey and its derivatives before dehydration. Compared to vacuum evaporation, the energy consumption is lower, however, the concentration level is limited to about 25–28 % dry matter (VRF 4) due to the increase of osmotic pressure and viscosity and in order to avoid salt precipitation and lactose crystallization.

As the high salt content of whey decreases its nutritional value and generates processing difficulties, demineralization of whey is carried out before drying. Electrodialysis (ED) and/or ion-exchange chromatography (IEC) are currently

used to achieve demineralization of whey in the range 50–90 %. However, as the whey to be demineralized should be previously concentrated by RO, these techniques involve high investment and running costs and generate large volumes of polluting effluents. On the contrary, nanofiltration (NF) appears to be more attractive even if this process leads to a lower level of demineralization. NF permits to concentrate and demineralize the whey simultaneously at low transmembrane pressure. The process is thus more cost-effective and environmentally friendly compared to ED and IEC. In addition, as nutrition value ions such as calcium are more retained by the membrane than monovalent ions (such as Cl^-), the final products show higher nutritional and technological properties.

Fractionation of White Wine Proteins by Membrane Operations

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Fractionation is a separation process in which a certain amount of a mixture is divided up into a smaller number of quantities or fractions with different molecular composition. Fractionation is based on the difference in specific properties between the individual components. Commonly equilibrium has to be aimed between the recovery of a specific compound and the desired purity of each fraction.

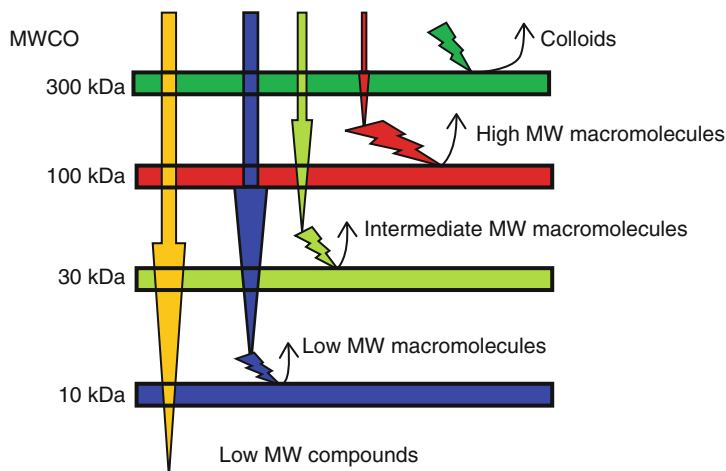
Proteins from white wines differ in molecular weight, ranging from 9 to 72 kDa, isoelectric point with pI between 3 and 9, hydrophobicity, degree of glycosylation, and thermal stability. Proteins can exhibit positive effects such as the stabilization of foam in sparkling wines, the interaction with aroma compounds, the protection of wine against precipitation of tartaric salts, and the interactions with other wine compounds such as

ethanol, polyphenols, and polysaccharides. However, they are also involved in some aspects that can impair the acceptance of the final product by consumers, such as haze formation during bottle storage and wine allergy (Ferreira et al. 2002). Therefore, several fractionation methods have been developed to achieve a selective separation of wine proteins.

First some preparative separation methods are often used such as dialysis (3.5 kDa cutoff membranes) to eliminate low molecular weight compounds, ultrafiltration (10 kDa cutoff membranes) to isolate and concentrate proteins, or protein precipitation by adding high concentration of salts (ammonium sulfate) or organic solvents (ethanol, methanol, or acetone). Afterwards, several chromatographic, electrophoretic, and membrane separations are usually combined that results into enriched protein fractions. A number of different chromatographic techniques, such as ion exchange, gel filtration/size exclusion, hydrophobic interaction, affinity, and chromatofocusing, have been developed for the fractionation and purification of wine proteins. In addition to chromatographic techniques, electrophoresis such as capillary electrophoresis and capillary gel electrophoresis can be used to achieve protein fractionation on a preparative scale (Le Bourse et al. 2010).

Sequential fractionation of white wines (Fig. 1) by using a series of ultrafiltration membranes with decreasing molecular weight cutoff ranging from 300, 100, 30 to 10 kDa allows to study foam stability of champagne wines (Abdallah et al. 2010) and protein haze stability of white wines (De Bruijn et al. 2011a, b). Ultracel PLC membranes of composite regenerated cellulose within a stirred frontal cell or a cross-flow unit should be preferred due to their ultralow protein binding capacity. Although the purity of protein fractions improves during membrane fractionation, a decrease of protein stability has been observed due to the retention of high macromolecular species (glycoproteins superior of 100 kDa) by the ultrafiltration membrane. This changing composition of the wine matrix makes membrane fractionation a complex process.

Fractionation of White Wine Proteins by Membrane Operations,
Fig. 1 Protein fractionation by ultrafiltration membranes



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Free Diffusion

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Free diffusion is a random nonrestricted walk or shift of atoms, ions, or particles on distances higher than those of the interatomic ones. From the atomistic point of view, diffusion is considered

as a result of the random walk of the diffusing particles, self-propelled by thermal energy (Brownian motion); from the phenomenological (macroscopic) point of view, such (diffusion) flux, which can be described by Fick's laws, is proportional to the minus gradient of chemical potential and goes from regions of higher concentration to regions of lower concentration of diffusant in appropriate (motionless) environment or solvent till concentration equalizing. From thermodynamic point of view, diffusion (mixing) in chemical system increases its entropy (a rate of disorder) and tends to state with the lowest inner energy.

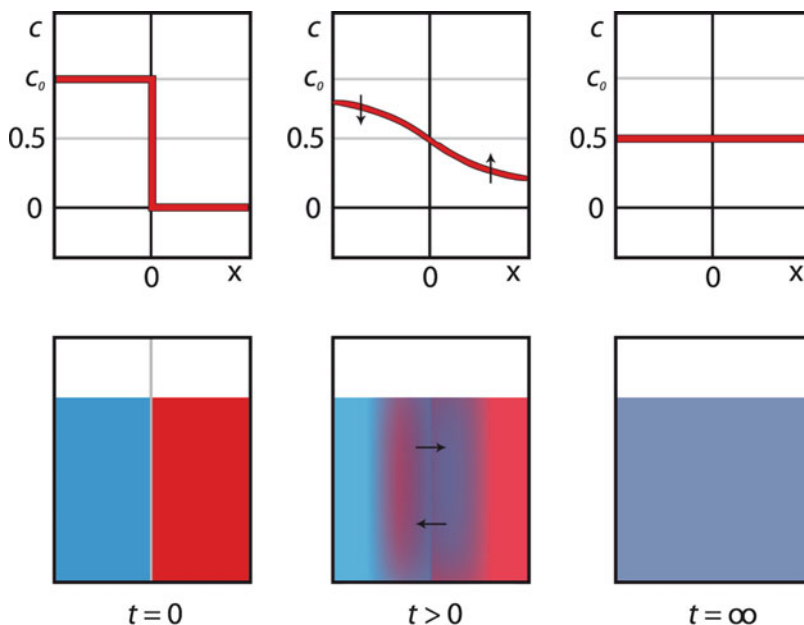
An example of free diffusion is as follows (see Fig. 1). If we consider infinite cylinder of unit cross section, not with an instantaneous plane source at $x = 0$, but with an initial distribution of concentration given by $c = c_0$ for $x < 0$ and $c = 0$ for $x > 0$, at time $t = 0$, solution of the *Fick's second law* in the one-dimensional case (coordinate x) after several treatment steps and substitutions gives a solution in the form (Jost 1960; Cranck 1975)

$$c = \frac{c_0}{2} \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (1)$$

where $\operatorname{erf} x$ is Gauss error function ($\operatorname{erf}(-x) = -\operatorname{erf}(x)$; $\operatorname{erf}(\infty) = 1$) and D is a diffusion coefficient. Thus, with if we imagine at $t = 0$ in cylinder (column) one solution with diffusing species with its concentration $c = c_0$ (at $x < 0$) and a second solution (pure solvent) with $c = 0$ (at $x > 0$) given in contact (with sharp

Free Diffusion,

Fig. 1 Schematic draw of free diffusion with two solutions: a change of concentration profile in time given by Eq. 1 from time $t = 0$ (left) to $t = \infty$ (right)



interface at $x = 0$). If such system is kept at stable conditions (constant temperature and no vibrations from outside which could cause convection), at times $t > 0$ a former sharp interface tends to vanish due to diffusion between both solutions, and at long times ($t = \infty$) concentration in the whole system became identical and is equal to the half of the initial concentration $c = c_0/2$.

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Free NaA Stabilized Sodalite (SOD)

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Sodalite (SOD) is a small-pore (2.8 Å) zeolite and so good candidate in the separation of small molecules such as NH_3 (2.55 Å), He (2.6 Å), H_2O

(2.65 Å), and H_2 (2.95 Å) from gas or liquid mixtures (Khajavi et al. 2007). In 1969 aluminosilicate sodalite was first synthesized using tetramethylammonium as structure directing agent (SDA) (Baerlocher and Meier 1969). For the first time, Bibby and Dale successfully reported the synthesis of silica sodalite (Bibby and Dale 1985). They prepared silica sodalite using a nonaqueous solvent. In particular, the ethylene glycol was used as solvent and SDA and the unit cell composition obtained was $\text{Si}_{12}\text{O}_{24} \cdot 2\text{C}_2\text{H}_4(\text{OH})_2$. Subsequently, it demonstrated the possibility to prepare silica sodalite by using SDA 1,3,5-trioxane (Keijsper et al. 1989). Recently, Yang and coworkers studied the effect of water in a solvothermal system composed of SiO_2 , NaOH, and ethylene glycol. They discovered a little amount of water did not influence the sodalite crystallization (Yang et al. 2007). However, when the water molar exceeds the silica one, the a-quartz phase was synthesized. The authors also demonstrated the addition of germanium into the system accelerated the crystallization of SOD. These and other SDAs (Braunbarth et al. 1997; Werthmann et al. 2000) can be used to synthesize sodalite crystals. However, for each SDA the optimization of the synthesis conditions is required above all the temperature that can be varied from

some days to different weeks (Münzer et al. 2008). Considering the pore size of this zeolite, different research groups tried to prepare sodalite membranes for the separation of small molecules. For example, low silica SOD membranes were prepared by microwave-assisted hydrothermal synthesis (Julbe et al. 2003). The prepared membranes exhibited a low He/N₂ permselectivity (6.2) owing to the presence of intercrystalline defects into the zeolite layer. Recently, defect-free supported hydroxy sodalite membranes were hydrothermally synthesized on alumina disk and used in pervaporation (Khajavi et al. 2010). The membranes exhibited exceptional acid and base stability within a pH range of 2.7–13.7 as confirmed by the very high water selectivity values (1,000,000) and stable fluxes.

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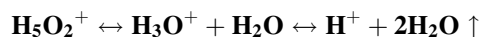
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Free Protons in Solid Heteropoly Compounds

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The basic structure of hetropoly acid hydrates (HPAs·nH₂O) has already been determined by Keggin (1934), but the water and hydrated proton entities filling the channels (secondary structure) have not been studied much until the early 1990s. As heteropoly acids are superionic proton conductors at room temperature and good catalysts, it is clear that their activities will be the function of hydration degree and dynamics of proton species. Therefore, it was necessary to focus on the studies that identify protonic entities and follow their dynamics. The studies started on WPA-6, the most stable hydrate of WPA with well-known structure. Crystallographic results for WPA-6 show that Keggin's anions in WPA-6 are stabilized by dioxonium ion H₅O₂⁺, which was defined as planar and rigid (Brown et al. 1970). On the other hand, IR and Raman spectra taken at room temperature have shown that different protonic species (H₅O₂⁺, H₃O⁺, H₂O) exist in dynamic equilibrium (Mioč et al. 1991, 2005; Colombari and Tomkinson 1997):

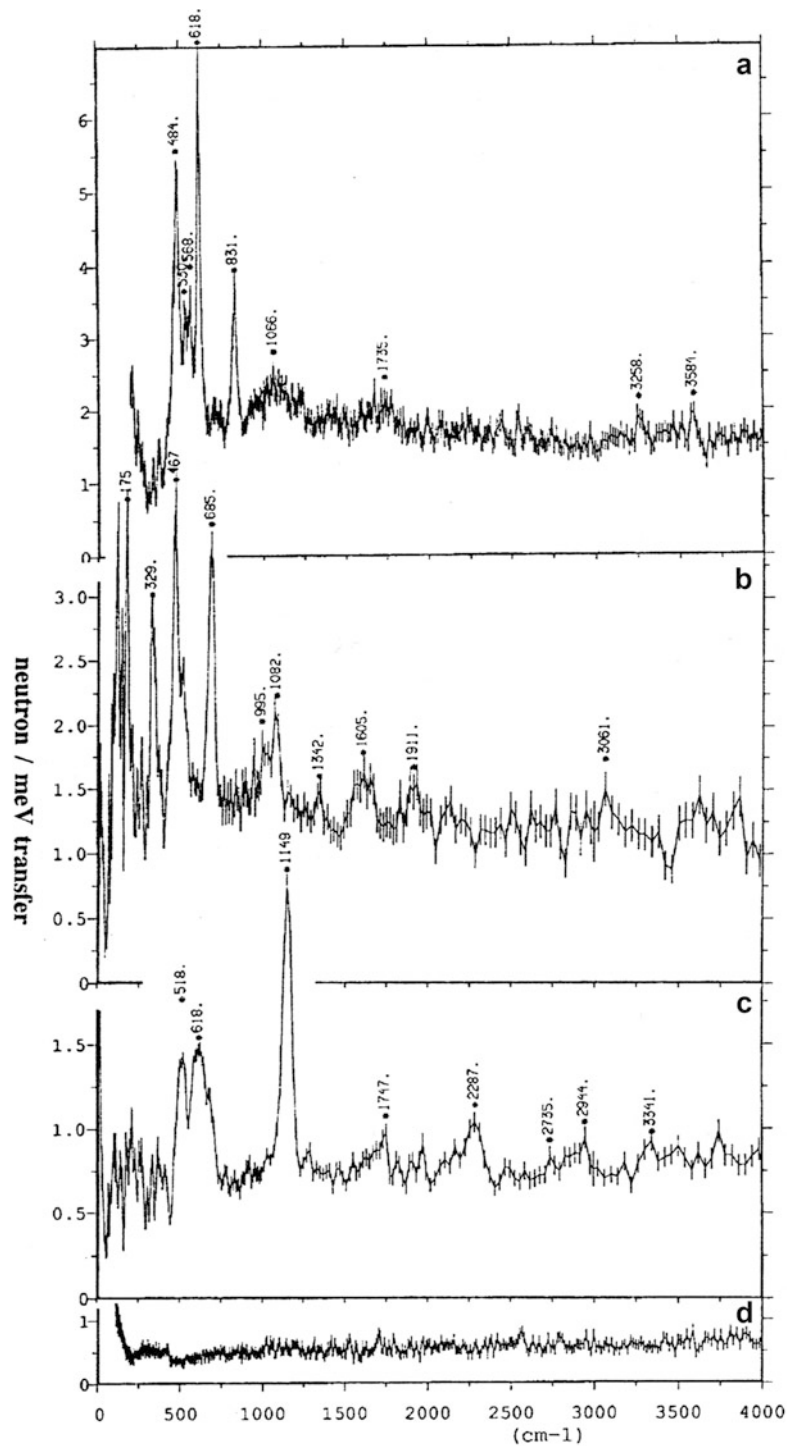


Spectroscopic results have also shown that dioxonium ion is not rigid, and even more, four conformation forms of the H₅O₂⁺ have been found (Kremenović et al. 2002). Theoretical ab initio calculations have proved that too (Mioč et al. 2008).

Finally, to confirm the proposed equilibrium, incoherent inelastic neutron spectra (IINS) were measured (Mioč et al. 1994; Fig. 1). Spectra of WPA-6 show that all bands characteristic of the abovementioned protonic species are present in IINS spectrum (Fig. 1a), and results are in accordance with literature data (Jones et al. 1989;

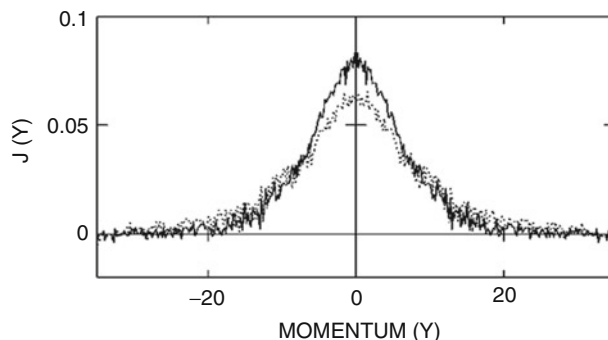
Free Protons in Solid Heteropoly Compounds,

Fig. 1 IINS spectra of WPA-6 (a), WPA-1 (b), WPA-0.2 (c), and WPA-D (d) (Reprinted with permission of Elsevier)



Free Protons in Solid Heteropoly Compounds,

Fig. 2 Compton profile of proton. Momentum distribution of single proton. Solid line for WPA-6 and dotted for WPA-0 (Reprinted with Permission of Elsevier)



Kearley et al. 1990; Tomkinson 1992). Changes in IINS spectra during the process of calcinations of WPA-6 are also evident (Fig. 1). When dehydration is completed, only protons stabilize the Keggin's structure, as was postulated. The IINS spectrum of WPA-0.2, calcinated at about 300 °C, was characterized by three main bands at 1149 ($0 \rightarrow 1$), 2287 ($0 \rightarrow 2$), and 3341 cm^{-1} ($0 \rightarrow 3$). The single strong band in the spectrum of the dehydrated phase at $1,149 \text{ cm}^{-1}$ was assigned to a proton centered within a symmetric (octahedral) environment of oxygen atoms. The obtained spectrum is very similar to that observed for manganese oxide ($\gamma\text{-MnO}_2$) where Fillaux identified “free protons”/“proton gas” for the first time (Fillaux et al. 1991).

Some additional neutron measurements were done at Rutherford Appleton Laboratory on the VESUVIO installation with high-energy (few eV) neutrons, with the aim to get more information about proton dynamics. From Fig. 2, it is evident that Compton scattering of protons takes place in the attosecond time scale. The “free protons” present in WPA-6 and those remaining in WPA-0.2 have a different single-proton momentum distribution (Fig. 2).

Using Born-Oppenheimer approximation (Chatzidimitriou-Dreismann et al. 2002), kinetic energy of chemical covalent bond formations was calculated in WPA-6 and WPA-0.2: E_{kin} (WPA-6) = 174 meV and E_{kin} (WPA-0.2) = 231 meV. Results show that protons are more spatially localized in WPA-0 than in WPA-6 phase on the time scale of 10^{-14} s. Ratajczak et al. discussed the obtained neutron results and compared them with those of

Kozhevnikov obtained by ^{17}O NMR spectroscopy (Ratajczak et al. 2001, pp. 100–117). Kozhevnikov (1998) speaks also about over-coordinated protons in case of HPAs but in tetrahedral surrounding of oxygen atoms. He has emphasized the important role of “free protons” in acid catalysis. A short time later, Essayem also discusses the role of “free protons” in acid catalytic processes and activity of Cs-WPA salt ($\text{Cs}_{1.5}\text{H}_{1.1}\text{PW}_{12}\text{O}_{40}$) (Essayem et al. 2000). Some other authors, as Janik et al. (2004), also speak about “free protons” and deprotonated water formed from protons and few oxygen atoms from Keggin's anions. Recently, Ph. Colomban continues to emphasize the importance of protons in solids (Ph. Colomban 2013). It could be said that nowadays the idea of “free protons” in solids is accepted in the scientific community.

Ratio of $\text{H}^+/\text{H}_2\text{O}$ and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ is also very important for conductive characteristics of these compounds as charge carriers and species forming networks of hydrogen bonds responsible for fast proton transport, i.e., high proton conductivity (Table 1). Many things could be analyzed from data concerning proton conductivity: influence of degree of hydration, influence of protonic ratio, and influence of big cations, in the case of salt on water dissociation. It is evident that cation parameters influence both the host lattice and rearrangement of protonic entities and their dynamics. In the last row are some data for $\text{KH}_2\text{PW}_{12}\text{O}_{40} \cdot 7\text{H}_2\text{O}$ (KH_2WPA) which have been used as PEM in H_2/O_2 fuel cell with very promising results (Holclajtner-Antunović et al. 2010).

Free Protons in Solid Heteropoly Compounds, Table 1 Proton conductivity of some HPCs

Compound	Conductivity (S/cm ⁻¹)
H ₃ PW ₁₂ O ₄₀ ·29H ₂ O	8.0·10 ⁻²
H ₃ PW ₁₂ O ₄₀ ·21H ₂ O	3.4·10 ⁻³
H ₃ PW ₁₂ O ₄₀ ·6H ₂ O	1.25·10 ⁻⁵
H ₃ PMo ₁₂ O ₄₀ ·29H ₂ O	0.13
H ₃ PMo ₁₂ O ₄₀ ·14H ₂ O	1.0·10 ⁻⁴
H ₄ SiW ₁₂ O ₄₀ ·30H ₂ O	2.5·10 ⁻³
Li ₃ PW ₁₂ O ₄₀ ·27H ₂ O	1.25·10 ⁻²
Na ₂ HPW ₁₂ O ₄₀ ·15H ₂ O	1.7·10 ⁻⁴
Na ₃ PW ₁₂ O ₄₀ ·16H ₂ O	6.6·10 ⁻⁵
K ₃ PW ₁₂ O ₄₀ ·10H ₂ O	1.7·10 ⁻²
Rb ₃ PW ₁₂ O ₄₀ ·6H ₂ O	1.7·10 ⁻²
Cs ₃ PW ₁₂ O ₄₀ ·8H ₂ O	2.5·10 ⁻²
MgHPW ₁₂ O ₄₀ ·27H ₂ O	1.26·10 ⁻²
MgHPW ₁₂ O ₄₀ ·14H ₂ O	1.0·10 ⁻²
CaHPW ₁₂ O ₄₀ ·21H ₂ O	5.0·10 ⁻³
BaHPW ₁₂ O ₄₀ ·7H ₂ O	2.0·10 ⁻³
BaHPW ₁₂ O ₄₀ ·13H ₂ O	1.6·10 ⁻²
K ₃ WPA·7.6H ₂ O	8.7·10 ⁻⁵
K ₂ HWPW·7.4H ₂ O	7.2·10 ⁻⁵
KH ₂ WPA·7.3H ₂ O	1.4·10 ⁻⁴
KH ₂ WPA·7H ₂ O	1.0·10 ⁻²
(t = 80 °C; RH = 70 %)	

The existence of different protonic species in HPCs·nH₂O was confirmed by dielectric measurements from Cole-Cole diagrams ($\epsilon'' = f(\epsilon')$) too. Debye's type relaxation times were determined in two frequency regions: from 5 to 500 kHz and in microwave region from 8 to 12 GHz. The relaxation time of 1.0×10^{-10} was assigned to the reorientation H₃O⁺ ion and/or H₂O molecules; and relaxation time of 1.6×10^{-8} s was ascribed to the H⁺ and/or H₃O⁺ reorientation and that 1.0×10^{-11} to proton jumps (Tjapkin et al. 1993). With temperature increase, the relaxation times are changing in function of proton entities participated in dehydration process.

Whatever we call protons in solids, “free protons,” “proton gas,” or over-coordinated protons, it is a special, new state of protons in solids, not only in HPCs, forming covalent bonding on a time scale of 10^{-13} to 10^{-15} s, which determines their catalytic and conductive characteristics.

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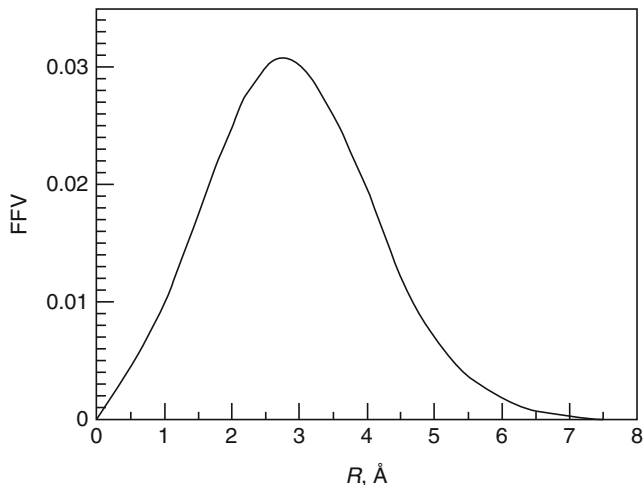
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Free Radical Polymerization

► Surface Modification: Wet Chemical Oxidation

Free Volume Distribution, Fig. 1 Size distribution (MD) of free volume in 6FDA-3MPD polyimide accessible for o-positronium probe (Adopted from Heuchel et al. (2004))



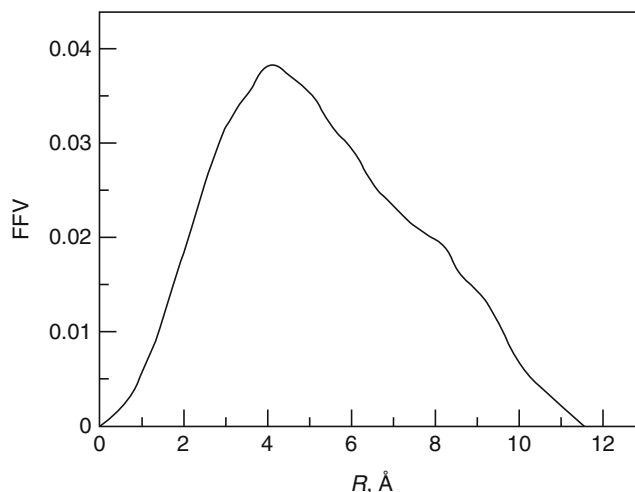
Free Volume Distribution

Yuri Yampolskii

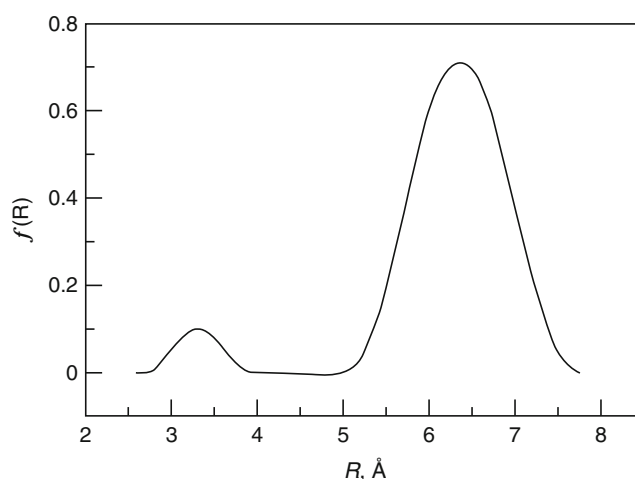
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Size distribution of *free volume* in glassy membrane materials is accessible to estimation by computer simulations (*molecular dynamics*, MD) and to experimental studies by the probe methods. In low permeable and highly selective conventional glassy polymers like polyimides, size distribution of free volume elements (microcavities), according to MD, is located within the range of microcavity radius 1–5 Å and can be represented by the Gauss function (Heuchel et al. 2004) (see Fig. 1). For polymers with greater gas permeability such as *poly(trimethylsilyl propyne)* (PTMSP) or amorphous Teflon AF, according to MD, it is much wider and extends up to microcavity radius 10–12 Å (Hofmann et al. 2003) (see Fig. 2). *Positron annihilation lifetime spectroscopy* (PALS) also indicates widely distributed sizes of free volume in highly permeable polymers. However, there are two interpretations of wide size distribution. According to Shantarovich et al. (1993)

Free Volume Distribution, Fig. 2 Size distribution (MD) of free volume in PTMSP accessible for o-positronium probe (Adopted from Hofmann et al. (2003))



Free Volume Distribution, Fig. 3 Size distribution (PALS) of free volume in PTMSP (Adopted from Hofmann et al. (2002))



and Consolati et al. (1996), lifetime distribution can be represented by bimodal size distribution (Fig. 3), while Dlubek (2008) proposed to consider monomodal size distribution with variable dispersion. Both approaches are consistent with the results of MD simulation.

Cross-References

- [Dynamic Free Volume](#)
- [Fractional Free Volume \(FFV\)](#)

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Free Volume Element

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Free volume element (FVE) (synonyms: microcavity, hole) is a conditional notion used for description of free volume in polymers (mainly in glassy polymers). Thus, in the positron annihilation lifetime spectroscopy (PALS) (Shrader and Jean 1988; Bartos 2000), it is defined as a sphere with the diameter R estimated using the Tao-Eldrup equation (Tao 1972; Eldrup et al. 1981) via the o-positronium lifetimes τ_i . In this approach it is conceived that polymer can be considered as a continuous matrix with uniformly distributed in it spheres with the size $4/3(\pi R^3)$. It was also assumed that cylindrical shape of FVE is a more realistic representation, so corresponding equation for calculation of the volume of FVE was proposed (Goworek et al. 2000). The PALS method permits an estimation of the mean concentration of FVE or hole number density N - (Dlubek et al. 2003). In all the polymers, the N values are limited within relatively narrow range of $(2-8) \cdot 10^{20} \text{ cm}^{-3}$ at the glass transition temperature T_g (Dlubek et al. 2003; Yampolskii 2010). Computer modeling of polymers indicates that the use of FVEs dispersed in dense continuous matrix is only a convenient oversimplification. In reality the nanostructure of polymers is better approximated as a more or less continuous form of free volume, though the sizes of FVEs get within the size distribution of free volume according to molecular dynamics (Hofmann et al. 2003).

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Free Volume Estimation

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Originally, *free volume* was interpreted (H. Fujita, M.H. Cohen and D. Turnbull, J.S. Vrentas and J.L. Duda) as an abstract parameter that fits the equation of *free volume model*. The methods for quantitative determination of free volume were proposed by S. Sugden and later by A. Bondi (1968). According to the latter, free volume V_f (cc/g) can be estimated as the difference: $V_f = V_{sp} - V_{occ}$, where the specific volume is defined as $V_{sp} = 1/\rho$ (ρ is the polymer density), while occupied volume V_{occ} can be found as $1.3 V_w$, where V_w is the *van der Waals volume* of the repeat unit of the polymer. The V_w value can be estimated from the increments tabulated for various groups (Van Krevelen and te Nijenhuis 2009). The factor 1.3 is taken from the packing density of molecular crystal at 0 K (accounting for inaccessible volume). Bondi's formula was criticized: the factor 1.3 might not be a universal constant, applicable in all cases; V_w of repeat units cannot be considered as the sum of increments of the groups that form

it. However, V_f value found using this formula is a simple and convenient measure of free volume in polymers (especially glassy) and it found a wide use. Often, it is more convenient to use a dimensionless value, *fractional free volume* FFV defined as V_f/V_{sp} . It is widely used in many correlations. In most polymers, FFV is in the range 0.1–0.25; however, there are examples where it reaches the value of 0.35.

Since the 1990s, several experimental methods (so-called probe methods) appeared and started to be used for the direct estimation of free volume in polymers (Yampolskii 2007). Among these methods (inverse gas chromatography, ^{129}Xe -NMR, and others), the most accepted and reliable one is the *positron annihilation lifetime spectroscopy* (PALS) (Dlubek 2008). It is based on the measurement of annihilation lifetimes of o-Ps (hydrogen-like atom formed by electron and positron): the longer its lifetime, the larger is the microcavity in the polymer where it resides and annihilates. The method permits estimation of discreet lifetimes or its distribution (hence, size distribution of microcavities). In conventional glassy and rubbery polymers, the radius of microcavity R (it is assumed that it has spherical geometry) is in the range 0.2–0.3 nm; however, in highly permeable polymers, it can be as large as 0.7 nm. In conventional polymers, o-Ps lifetime distribution and *free volume size distribution* is monomodal (Gauss-type distribution). In highly permeable polymers, it is, as a rule, bimodal with prevailing larger microcavities. By combining PALS and PVT data, it is possible to estimate the concentration of microcavities or hole number density N (Dlubek 2008). In all polymers, the N values are in the range 10^{20} – 10^{21} cm^{-3} . It is possible also to calculate PALS-based $\text{FFV} = N(4/3)\pi R^3$. Different probe methods give the radii of microcavities in rather good agreement (Yampolskii 2007).

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Free Volume Model

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The concept of free volume is extensively used in respect of various properties of condensed phases. Regarding nonporous polymeric membranes, it is quite useful in the description of diffusion phenomena. The model proposed by Cohen and Turnbull (1959) for transport in liquids and amorphous glasses considers a matrix consisting from hard molecules. It gives the following equation for the diffusion coefficient as a function of average free volume per molecule v_f : $D = A \exp(-\gamma v^*/v_f)$, where A is the constant, γ is the constant that takes into account possible overlapping of microcavities, and v^* is the minimum required volume of microcavity and often is considered as the size of the diffusing molecule. A modified equation was proposed later by Fujita (1961) where instead of v_f , the fractional free volume (FFV) was used:

$D = A_d R T \exp(-B_d/\text{FFV})$. It is accepted that the constants A_d and B_d depend on the nature (size) of the diffusants. These equations are valid only when the concentration of penetrants is small and they do not exert perturbation on polymer matrix (e.g., swelling). In transport of organic vapors, much more complicated equations were proposed and used (Vrentas et al. 1977; Petropoulos 1994). It is important that these equations include an activation term $\exp(-E_j/RT)$, where E_j is the energy needed for the diffusing molecule to jump into the next hole.

Free volume found using either of abovementioned models usually shows good

correlations with the diffusion coefficients of gases in polymers and often with the gas permeability coefficients. The concept of free volume was strongly enriched by the use of contemporary simulation methods (molecular dynamics, molecular mechanics, and Monte Carlo) and experimental probe techniques. However, in many cases (especially for highly permeable polymers), it is important to supplement the consideration with information on connectivity (openness) of free volume (Willmore et al. 2006).

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Freundlich Isotherm

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A Freundlich isotherm is a mathematical expression for the adsorption equilibrium between a fluid (liquid or gas) and a solid material. The Freundlich equation is an empirical expression representing the isothermal variation of adsorption of a liquid or gas onto the surface of a solid material, derived by Freundlich (1909) as an empirical relation.

For adsorption of a gas as the adsorbate to a solid adsorbent, the following equation represents a Freundlich isotherm:

$$\frac{x}{m} = kP^n \quad (1)$$

In this equation, x is the adsorbed quantity, m is the mass of the adsorbent, P is the partial pressure of the adsorbate in the gas, and k and n are empirical constants for each adsorbent-adsorbate pair at a given temperature.

For adsorption of a liquid, the relation between the adsorbed amount per gram of the solid at equilibrium Q (mg/g) and the concentration C in solution at the equilibrium (mg/l or $\mu\text{g/l}$) is given by the following equation:

$$Q = K.C^n \quad (2)$$

in which K and n are constants at a given temperature.

When the Freundlich equation is written in logarithmic form, a linear relation between $\log Q$ and $\log C$ is obtained:

$$\log Q = \log K + n \log C \quad (3)$$

Freundlich isotherms are often used to describe adsorption equilibria between a membrane and a feed solution. This is essential for the description of phenomena such as membrane fouling (Van der Bruggen et al. 2002) and breakthrough effects due to desorption (McCallum et al. 2008) in aqueous solutions. Desorption of adsorbed organic compounds to the permeate may result in negative apparent rejections when the concentration of the organic compound in the membrane phase is larger than the equilibrium permeate concentration given by the Freundlich isotherm. The permeate concentration during this unsteady-state filtration period is similar to breakthrough curves encountered in the description of adsorption columns. Kimura et al. (2003) demonstrated that adsorption of hydrophobic compounds, which can be described by the Freundlich equation, might lead to underestimation of the permeate concentration (or overestimation of rejection) due to saturation of the membrane and subsequent desorption. This is very important in the translation of experimental results to real scale applications. Thus, a fundamental understanding of adsorption is a prerequisite.

Adsorption equilibria using the Freundlich isotherm can also be used for membrane

characterization. Ge et al. (2006) demonstrated that the variation in membrane thickness and pore size can be predicted by studying Freundlich isotherms. They found that when the variations were larger, the time of total saturation is delayed, the loading capacity at the point of breakthrough decreases, the solute recovery efficiency and ligand utilization efficiency decrease, and the thickness of unused membrane increases.

The Freundlich isotherm is often used because of its simplicity and wide applicability. However, other isotherms can also be used to describe adsorption on membrane surfaces. The most commonly applied are the Langmuir isotherm and the BET equation. The Langmuir model was derived theoretically by Irving Langmuir in 1916 as a mathematical expression for monolayer adsorption onto a solid surface. Although this model has a theoretical basis, its application is limited to monolayers; in addition, the Langmuir model does not work well for rough surfaces, which is often the case for membranes. The Langmuir model was extended in 1938 by Stephen Brunauer, Paul Emmett, and Edward Teller, who developed a new theoretical model for multilayer adsorption that became known as the BET model (as an acronym for Brunauer-Emmett-Teller). Although more complex than the empirical Freundlich equation, it has the advantage of a strong fundamental basis, which goes beyond the simple approximation in the Freundlich model.

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Fruit Juice Processing by Integrated Membrane Operations

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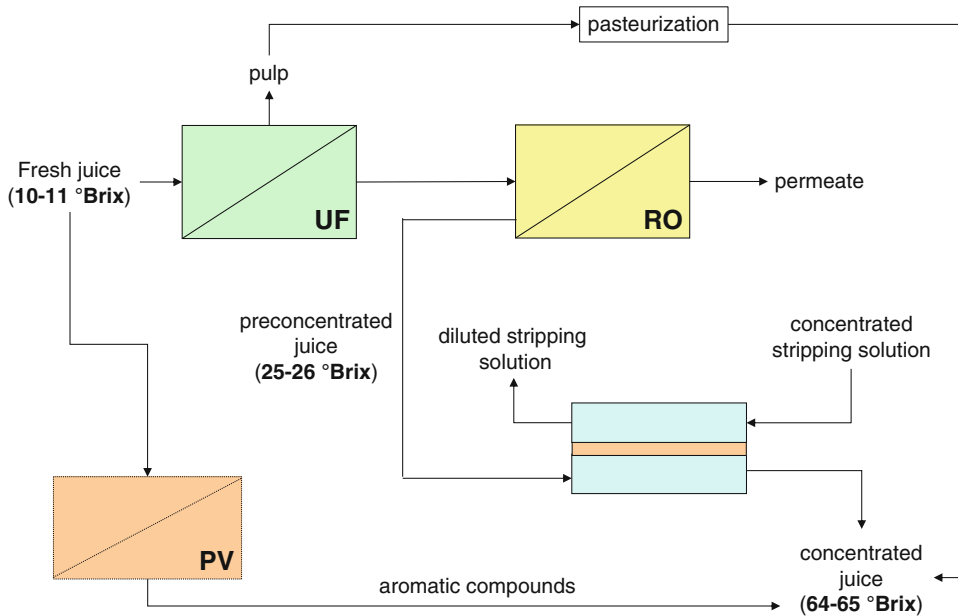
Fruit juice clarification, stabilization, depectinization, and concentration are typical steps where membrane processes such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), osmotic distillation (OD), and membrane distillation (MD) can be utilized as alternative technologies to the conventional transformation technologies. Particularly, MF and UF are valid approaches for the clarification of fruit juices as alternative to the use of fining agents, such as gelatin, diatomaceous earth, bentonite, and silica sol, which cause problems of environmental impact due to their disposal (Echavarria et al. 2011).

Clarified juices coming from MF or UF processes can be commercialized or submitted to a concentration process in order to obtain a product suitable for the preparation of juices and beverages.

RO, MD, and OD can be used as concentration techniques as alternative systems to thermal evaporation or cryoconcentration (Jiao et al. 2004).

Integrated membrane operations have been suggested for replacement of conventional juice processing unit operations for the clarification and concentration of different fruit juices as well as for the recovery of aroma compounds.

A typical example of integrated membrane system for the clarification and concentration of fruit juices is depicted in Fig. 1. The fresh juice is clarified by UF; the clarified juice is pre-concentrated by RO and then concentrated by OD. Pervaporation (PV) is used to recover aroma compounds from the fresh juice.



Fruit Juice Processing by Integrated Membrane Operations, Fig. 1 Integrated membrane process for the production of concentrated fruit juice

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Fuel Cell Applications

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Fuel cell is an energy conversion device which converts chemical energy of a fuel directly into electricity which can be used for light, heat, and shaft power. Therefore in principle fuel cell can replace heat engines for stationary power

generation and transport applications. The main types of fuel cells are as follows (Table 1):

Different types of fuel cell have been developed for different applications. For example, solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) systems are used in stationary power generation or marine applications, whereas polymer electrolyte fuel cell (PEMFC) systems are chosen for automotive applications.

In the transport sector, the fuel cell has potential to replace internal combustion engine, and in the recent years, the use of fuel cell to power automobiles such as buses, motorcycles, train, boats, and airplanes has been demonstrated by various companies.

Fuel cell systems can generate power for distributed electricity (connected to grid) and grid-independent portable and small-scale generators for emergency and critical areas applications. Particularly for disaster areas and defense applications, fuel cell application is very attractive as fuel cell generates not only electricity, but it produces water also. Fuel cell plants prove to be very efficient for cogeneration, i.e., combined heat and power (CHP) for residential buildings or small communities as the waste heat can be utilized for

Fuel Cell Applications, Table 1 Fuel Cell Applications

Type	Electrolyte phase	Operating temperature	Electrolyte	Responsible ion
Molten carbonate fuel cell	Liquid electrolyte	500–650 °C	Molten carbonate	CO_3^{2-}
Phosphoric acid fuel cell		160–200 °C	Phosphoric acid	H^+
Alkaline fuel cell		60–220 °C	Liquid (KOH) immobilized	OH^-
Solid oxide fuel cell	Solid electrolyte	600–850 °C	Ceramic YSZ	O^{2-}
Polymer electrolyte fuel cell		–40–80 °C (120–180 °C HT)	Acid-doped solid polymer	H^+

heating. The fuel cell system for CHP varies between 2kWe for an individual house and 100kWe for small communities.

Portable fuel cell systems supply power in the same way as batteries and can also be used to charge batteries for small electrical devices.

Biofuel cells are at research stage, and several researchers are investigating their potential for generating electricity combined with applications such as waste treatment and metal recovery from waste streams.

Fuel Cell Components

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All fuel cells essentially consist of two electrodes – an anode (negative side) and a cathode (positive side) – and an electrolyte to allow charges to move between the two sides of the fuel cell. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. On both sides of the electrolyte and two electrodes (cathode, anode) are the catalyst layers. A catalyst lowers the activation energy to undergo a reaction and helps the reaction to take place at a faster rate. The fuel cell

type is defined based on the nature of the electrolyte. The six types are alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), proton exchange membrane or polymer electrolyte membrane (PEM) fuel cell, and solid oxide fuel cell (SOFC). The PEM and SOFC have solid electrolyte, while other three fuel cell types have liquid electrolyte. In a solid electrolyte fuel cell, for example, a PEMFC, the catalyst layer is spread either on the electrolyte (as in PEM or SOFC) or on the electrode. In addition to these basic components, other components are gas diffusion layer, electric connections, current collectors, separator plates, and seals. In PEM fuel cell bipolar plates made up of metal or conductive polymer (or carbon composites) have more than one function. Bipolar plates allow the transfer of electrons from the anode side of one cell to the cathode side of the adjacent cell, provide structural rigidity of the stack, distribute reactant gas to each cell within a stack, and distribute reactant gas within the cell in the stack through proprietary flow field topology (shape designs). In some cases, heat management can be integrated in BPP design which typically involves a thermally conductive medium being supplied through the stack to remove heat from the stack. Thermally conductive mediums typically can be air, de-ionized water, or a coolant with high specific heat capacity. Liquid electrolyte fuel cells will have electrodes immersed in the liquid electrolyte and often benefit from simplified design and also less expensive catalyst materials. As a result, liquid fuel cells, such as PAFC and MCFC, are well-established technologies and have been widely used for medium-scale

Fuel Cell Components, Table 1 Basic components of different fuel cells

Fuel cell type	Electrolyte	Electrolyte type	Catalyst
Alkaline	Solution of potassium hydroxide KOH	Liquid	Platinum
Molten carbonate	Sodium or magnesium carbonates (CO ₃)	Liquid	Nickel
Phosphoric acid	Phosphoric acid	Liquid	Platinum
Polymer electrolyte	Polymer electrolyte membrane	Solid	Platinum
Solid oxide	Ceramic compound of metal (like calcium or zirconium) oxides	Solid	Nickel

(<250 kW) stationary applications. Table 1 shown below gives an overview of each type of fuel cell, its electrolyte, and the primary catalyst used.

Fuel Cell Membrane

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Low-temperature fuel cells can be equipped with a proton or anion exchange membrane in alternative to liquid electrolytes (Aricò et al. 2001). The core of a polymer electrolyte fuel cell (PEMFC) is the ion exchange membrane. The electrodes (anode and cathode) are in intimate contact with the membrane faces. The membrane determines the fuel cell resistance and the fuel permeation rate, and it influences the reaction rate. It is well known that the use of non-noble metal catalysts is possible in the presence of alkaline electrolytes. Proton-conducting electrolytes have been preferred to alkaline electrolytes for several decades for practical reasons, e.g., to avoid carbonation.

The standard electrolyte membrane is usually a perfluorosulfonic acid membrane such as Nafion. Most of the electrolytes alternative to Nafion both proton conducting and alkaline type, e.g., hydrocarbon type, are significantly cheaper, and, in some cases, they are also characterized by smaller hydrogen and methanol crossover. However, lifetime characteristics similar to those shown by Nafion-type membranes in fuel cells have not yet been demonstrated for the alternative membranes. Concerning with the conductivity, only recently, membranes alternative to Nafion type have shown similar levels of performance. One critical aspect is related to the fact that the presence of water is a requirement of low-temperature PEMFCs and DMFCs for the occurrence of the electrochemical reactions and for the promotion of ionic conductivity (water-assisted conductivity mechanism). High ionic conductivities are often associated to the presence of large water uptake by the membrane, but this property often causes poor mechanical characteristics such as large swelling and relevant crossover (especially methanol). Phosphoric acid-doped polybenzimidazole membranes use a Grotthuss mechanism of proton transport and do not require water (Wang et al. 1995). These membranes operate at about 180–200 °C, whereas composite perfluorosulfonic acid membranes or sulfonated hydrocarbon membranes including inorganic fillers such as silica rely on the water-assisted mechanism, but they can operate up to 145 °C, under particular conditions (3 bar abs pressure), due to the enhanced water retention of the filler (Aricò et al. 2003).

Composite recast Nafion® membranes containing inorganic fillers have been employed in high-temperature (~150 °C) direct alcohol (Aricò et al. 1998) and H₂ air fuel cells (Watanabe et al. 1996). These composite membranes were originally developed for reduced humidification operation in polymer electrolyte fuel cells (Watanabe et al. 1996) due to the enhanced water retention inside the membrane by the effect of the inorganic filler (Aricò et al. 1998). A further advantage of composite membranes relies in the barrier effect given by the inorganic filler for methanol crossover (Ren et al. 1996).

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Fuel production (pervaporation application)

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Fuel is any material that stores potential energy in a form that can be practicably released and used as heat energy. The conventional fuels refer to chemical fuels including fossil fuels and biofuels. Fossil fuels are hydrocarbons, primarily coal and petroleum (liquid petroleum or natural gas), formed from the fossilized remains. Biofuel can be broadly defined as solid, liquid, or gas fuel consisting of or derived from biomass.

Since the heightened concerns for cleaner air and more stringent environmental quality requirements for sulfur concentration in oil products, ultra-deep desulfurization from fuels, particularly from gasoline, has become a very important subject in petroleum refining industry. It is well known that sulfur removal from FCC gasoline can be achieved by catalytic hydrodesulfurization.

However, this hydrotreating process results in a significant reduction of octane number due to the saturation of olefins (Lin et al. 2009). Pervaporation has been given much more attention as a promising and feasible technology for desulfurization of gasoline since Grace Davison Company reported the pervaporation membrane-based S-brane process in 2002 (White et al. 2005). The sulfur components can be preferentially removed from the gasoline feed due to its higher affinity with and/or quicker diffusivity in the membrane. Pervaporation desulfurization demonstrates distinct advantages over conventional technologies such as low energy consumption, simple operation, and little reduction of octane number. The pervaporation membrane materials involved in desulfurization are mainly hydrophobic polymers including polyurethane (PU), polyurea/urethane (PUU), polyimide (PI), natural rubber and poly(styrene-co-butadiene) rubber, and polydimethylsiloxane (PDMS), as well as some hydrophilic polymers such as polyvinylpyrrolidone (PVP), cellulose triacetate (CTA), and polyethylene glycol (PEG) (Lin et al. 2009).

Among the variety of possible biofuels from the biorefinery, liquid transportation fuels in the form of bioethanol currently account for the vast majority of biofuels produced all over the world. A typical corn-to-ethanol production process consists of pretreatment of the starch to sugars with enzymes, fermentation of the sugars to ethanol with yeast, followed by distillation and dehydration processes of ethanol. Downstream from the fermentor is usually a dilute aqueous solution containing about 5–12 wt.% ethanol. Separation technologies such as pervaporation are applied for the subsequent ethanol/water separation. On the one hand, hydrophobic pervaporation membranes such as PDMS (Xiangli et al. 2008) and silicalite-1 zeolite membranes could be used for selective recovery of ethanol from fermentation broth. In addition, the fermentation process can be coupled with hydrophobic pervaporation membranes for in situ removal of the inhibitors (e.g., ethanol product and phenols) from the fermentation broth to realize the continuous fermentation. On the other hand, hydrophilic pervaporation membranes including PVA (Zhu et al. 2010) and NaA

zeolite membranes (Yang et al. 2012) could be used for dehydration of concentrated ethanol aqueous solution (usually containing 90–95 wt.% ethanol), obtaining the final bioethanol product.

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- The usual surface modifications in the literature are the following: coating (Dickson et al. 1998), self-assembly (Luo et al. 2005), chemical treatment (Van der Bruggen 2009), plasma treatment (De Geyter et al. 2008), and surface graft polymerization (Belfer et al. 2004).
- The coating is a physical surface modification that can be obtained via one of the following mechanisms:
- Adsorption/adhesion – the functional layer is only physically fixed on the base material; the binding strength can be increased via multiple interactions between functional groups in the macromolecular layer and on the solid surface.
 - Interpenetration via mixing between the added functional polymer and the base polymer in an interphase.
 - Mechanical interpenetration (macroscopic entanglement) of an added polymer layer and the pore structure of a membrane.

The main limitation of this method is that it does not allow to prepare membranes with stable surfaces because the new materials on the membrane surface run away easily.

Self-assembly technique permits to obtain supramolecular systems. It entails self-assembly monolayers (SAMs), in which it has the adsorption of an active surfactant on a solid surface and layer-by-layer (LBL) assembly in which the assembly is obtained by means of alternative adsorption of linear polycations and polyanions. The only condition for the use of the self-assembly method is that the base membrane must be able to adsorb the first polyelectrolyte layer by means of ionic bonds.

The chemical treatment permits to obtain membrane surface modification with functional groups rather stable. The modified membrane retains the original mechanical properties, while the interfacial properties are changed. The chemical modification is obtained using a chemical reaction such as oxidation, substitution, addition, and hydrolysis.

The plasma treatment permits to obtain membrane surface with different properties changing

Fully Fluorinated Polymers

► Amorphous Perfluoropolymers

Functionalized Membrane

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The functionalized membranes are membranes modified with appropriate functional groups that introduce new membrane properties, affinity or catalytic, for improving the selectivity or creating an entirely novel separation function (Ulbricht 2006).

parameter. Plasma gases are CF_4 , Ar, H_2 , He, Ne, N_2 , O_2 , and CO_2 , and the ionized gas can attack the C–C, C–H, and C–S bonds, excluding the aromatic C–C and C–H bonds. Surface modification with CO_2 plasma, generally, allows to obtain surface oxidation and the formation of hydrophilic surface; N_2 plasma makes amine, amide, imine, and nitrile functional groups on the membrane surface; and O_2 plasma leads to incorporation of oxygen containing functional groups such as hydroxyl, carbonyl, and carboxyl groups. Instead, to improve hydrophobic property of the membrane surface, high degree of fluorinated compounds such as SF_6 , CF_4 , and C_2F_6 are used as plasma gases.

Surface grafting is a chemical modification method. Compared with the physical methods such as coating, the covalent bond between the polymer chain and the membrane surface avoids the desorption phenomena maintaining the chemical stability of modified surface for long term. The grafting method is generally divided in two classes *grafting to* and *grafting from* based on different strategies of membrane functionalization. In the *grafting to* strategy, the polymer containing the reactive groups at the end or side chains is covalently coupled to surfaces, while in the *grafting from* strategy, an initiation, due to

active species on the membrane surface, permits the polymerization of monomer from the surface.

According to the different methods used for the surface activation, this technique is classified in chemical, radiation, photochemical, and plasma-induced grafting.

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Galacto-oligosaccharide Membrane Reactor

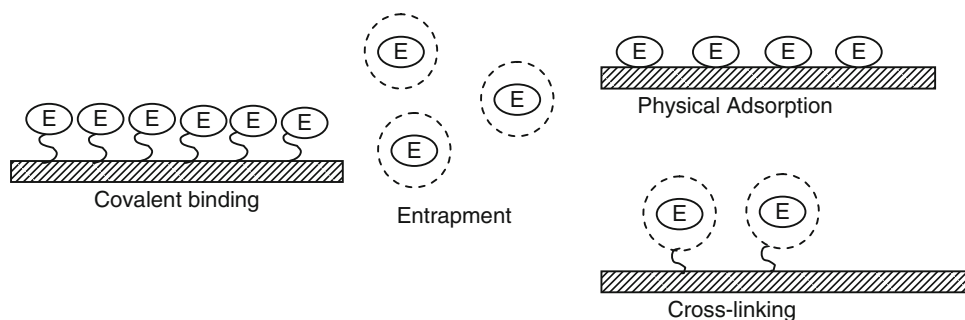
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One of the preliminary issues with galacto-oligosaccharide (GOS) synthesis in batch reactor is the retention of monosaccharides, glucose, and galactose, within the reaction medium that hinders the transgalactosylation (Chen et al. 2003) reaction pathway through competitive inhibition of enzyme β -galactosidase. Hence, the removal of these monosaccharides from the reaction medium reduces the possibilities of enzyme inhibition and, thereby, increases the yield of GOS (Sen et al. 2011). In accordance to do so, presently continuous membrane separation process following the reaction is one of the upcoming strategies that are being introduced in the process (Sen et al. 2011; Das et al. 2011). As a whole the technology has been referred as “enzymatic membrane reactor” (Das et al. 2011). One of typical approaches in enzymatic membrane reactor is immobilization of the enzyme over the membrane, as shown in Fig. 1, where the substrate comes in contact with the membrane and the

product will be formed subsequently. The concept of such immobilization was taking place in 1978 (Chibata 1978). The process of immobilization suggests several techniques attributing to adsorption/covalent linking of the biocatalyst on some inert solid support, encapsulation within some semipermeable matrix, or insertion of the biocatalyst within the matrix network (Rios et al. 2004). Snamprogetti S.p.A. (Italy) and Sumitomo Chemical (Japan) are some of the companies that are using enzyme immobilization technique to produce GOS from lactose (Grosová et al. 2008). Snamprogetti S.p.A. used *K. lactis* β -galactosidase entrapped in cellulose triacetate fibers by fiber wet spinning, while Sumitomo Chemical has developed high-purity immobilized β -galactosidase from *A. oryzae* covalently bounded to macroporous amphoteric ion-exchange resin of phenol formaldehyde polymer. The simplest form of enzymatic membrane reactor as described by Czermaka et al. (2004) is where the reaction was carried out in a CSTR followed by the separation of enzyme using 50 kDa molecular weight cut-off (MWCO) membrane. This ensures the separation and, thus, reutilization of enzyme during enzymatic hydrolysis of lactose. However, the criticality here is, as said before, the retention of monosaccharides within the reaction mixture might hinder the process by product inhibition even though with the subsequent membrane separation. Therefore, the researchers became concern to develop a reactor,



Galacto-oligosaccharide Membrane Reactor, Fig. 1 Different forms of enzyme immobilization



Galacto-oligosaccharide Membrane Reactor, Fig. 2 Enzyme immobilization on membrane

where simultaneous production and separation will be carried out. In view of this, Sen et al. (2012) had suggested a module that will simultaneously behaves as a production and purification unit for monosaccharides. According to the membrane reactor, enzyme β -galactosidase (from *B. circulans*) was immobilized over a 0.3 kDa nanofiltration thin-film composite polyamide membrane with an immobilization yield of 83 %. According to the protocol elaborated, the membrane surface was primarily hydrolyzed to generate free amine groups that are required to form a covalent bond with the glutaraldehyde with subsequent covalent linking with the polyethylenimine and enzyme (Fig. 2). According to them, it was found that with the membrane reactor, the GOS yield becomes almost double compared to GOS yield in batch reactor. Moreover, it has been reported elsewhere that water-soluble enzyme on bind with membrane potentially increases the enzyme activity depending on the membrane organization and topology of the binding (Sánchez et al. 2013). However, the performance of such enzymatic membrane reactor depends on the stability of the enzyme protein that might undergo some conformational changes because of unfolding of the protein or in other word denaturation of the protein (Iyer and Ananthanarayan 2008). With immobilization on

inert support, like membrane, possibility of such changes could be restricted with enhanced enzyme stabilization (Mateo et al. 2007). Furthermore, to reduce the possible sugar fouling of membrane reactor, Sen et al. (2012) suggested one indigenously fabricated module called rotating disk membrane bioreactor.

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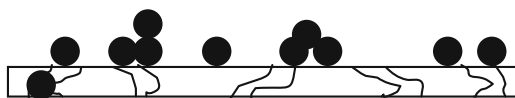
Galacto-oligosaccharide Production by Membrane Operations

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Membrane separation process is one of the mostly coveted applications in different segments of industries, especially, in food engineering and effluent treatment sectors. One of the substantial advantages that attributes to the membrane separation process is the separation of the macromolecules (with respect to the membrane) without much operational complexity. This ensures the reusability and high yield of the separated components as retentate. However, membrane separation process has some primal intricacies that sometimes constraint the application of the process, especially, in food processing industries as prominent technology. One of such complexities attribute to primarily membrane fouling (Fig. 1) that reduces the performance as well as the reusability of the membrane. Polysaccharides' fouling of the membrane is such a significant contributor



Galacto-oligosaccharide Production by Membrane Operations, Fig. 1 Fouling of membrane

to the foulant genre that might reduce the performance of the separation process (Metzger et al. 2007). Separation of galacto-oligosaccharides (GOS) from the reaction medium comprising of sugars and other saccharides using membrane separation technique could be one of the tempting issues in recent pasts that has been explored by food scientists. During membrane separation process, the primary objective that has to be decided by the user is the proper selection of membrane molecular weight cutoff (MWCO) and the membrane material itself that has low vulnerability toward the carbohydrate adsorption on the membrane. The molecular weight of GOS varies from di to penta units of monosaccharides (340–828 Da). However, formation of more than tri could be sometimes trivial because of the steric hindrance that resists attaching the mono-sugar unit with the galactosyl moiety (Chen et al. 2002). Hence, the nanofiltration with 300 Da membrane could be a better cutoff in separating GOS from other sugars present in the reaction mixture (Sen et al. 2011). Moreover, the membrane material is one of the key issues that control the yield of GOS. Sen et al. (2011) studied that polyethersulfone (PES) and cellulose triacetate (CTA) membrane could interact with the monosaccharides produced during enzymatic reaction and results an inhibition of the enzyme restricting the production of GOS. Aforesaid fouling of the membrane because of sugars and polysaccharides leads to an implementation of diafiltration, where the reaction mixture is continuously diluted with a volume of water (either in batch (Fikar et al. 2010) or continuous process) depending on the volume concentration factor (VCF) (given by the ratio of the feed volume and retentate volume after batch) maintained during the diafiltration. Grandison et al. (2002) studied the purification of produced GOS with two different nanofiltration membrane

modules, dead-end and cross-flow, in diafiltration mode and concluded cross-flow nanofiltration yields more purified GOS. In addition, they had compared their results with different sets of membrane, where they concluded thin-film composite membrane performs better than cellulose triacetate membrane in the purification of GOS. One of the reasons that attributes to an enhanced purification in cross-flow system is the sweeping action across the membrane, which removes the fouling layer of the deposited sugars on the membrane. In 2007, Mellal et al. had used multi-shaft rotating disk system in order to purify oligosaccharides to depict the applicability of high-sheared membrane modules. Das et al. (2011) had shown that nanofiltration with rotating disk membrane module, another high-sheared membrane module, will create enough turbulence over the membrane enough to disrupt the concentration polarization and yield purified GOS. Therefore, purification of GOS is one of the prime concerns that can be done with a convenient membrane separation scheme attributing to some mechanically modified low fouling devices.

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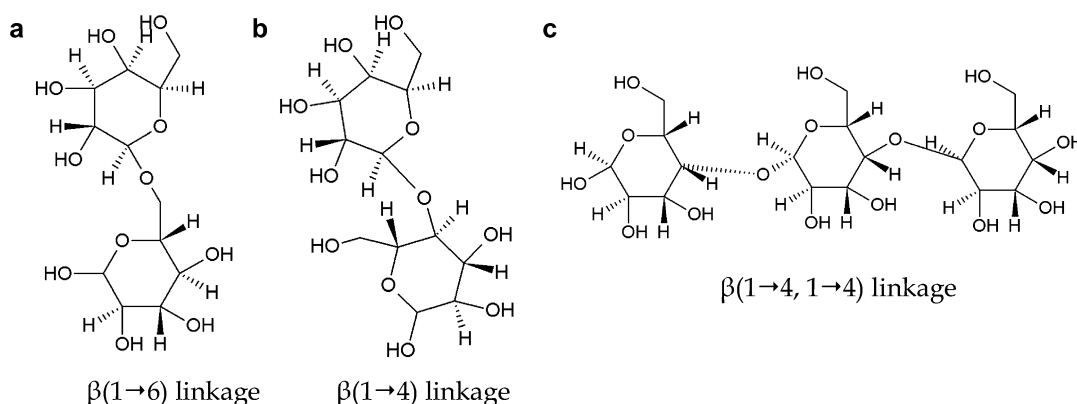
Galacto-oligosaccharides

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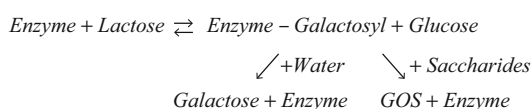
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Galacto-oligosaccharides (GOS), one of the potential prebiotic carbohydrates that are commonly produced from lactose using enzymatic hydrolysis, is basically composed of oligo-galactose with some lactose and glucose (Niittynen et al. 2007). It is produced by a hydrolytic action of β -galactosidase (EC 3.2.1.23) on lactose through transgalactosylation (Chen et al. 2003) reaction, and depending on the source of the enzyme, it comprises of different synthetic by-products' mixture. A typical application in the utilization of GOS is its medicinal usage as prebiotic food-based ingredient that aims to enhance the growth as well as metabolic activity of potentially health-promoting indigenous bacteria such as bifidobacteria and lactic acid bacteria (Depient et al. 2008). GOS can't be hydrolyzed in the small intestine attributed as an indigestible component within the intestine as lactose for lactose-intolerant person. However, intestinal bacteria such as *Bifidobacterium* or *Lactobacillus* species can ferment them to a production of short-chain fatty acids' salt acetate (metabolized by muscle), propionate (metabolized by the liver), and butyrate (metabolized by the colonic epithelium) (Rodriguez-Colinas et al. 2013). GOS is primarily composed of di-, tri-, tetra-, and pentasaccharides with galactose as the monomeric unit (Chen et al. 2003). Figure 1a–c is showing the GOS structures of different polysaccharides' units.



Galacto-oligosaccharides, Fig. 1 Different forms of GOS: (a) di-GOS with galactose-galactose (1 $\rightarrow$ 6) linkage, (b) galactose-galactose (1 $\rightarrow$ 4), (c) galactose-galactose-galactose (1 $\rightarrow$ 4;1 $\rightarrow$ 4) linkage

Production of GOS primarily depends on pH, substrate (lactose), and temperature of the enzymatic medium. However, as aforesaid, source of enzyme will be an obvious reason in the production of GOS yield as well as the condition of other parameters. As, for example, β -galactosidase derived from *Aspergillus oryzae* has GOS yield of 52 % with lactose concentration of 500 g/L, pH 4.5, and temperature 40 °C (Gosling et al. 2010), while in the enzyme obtained from *Kluyveromyces lactis* with 400 g/L lactose concentration, 7 pH, and 40 °C temperature, the yield was only 24.2 % (w/w) (Gosling et al. 2010). Other reason that has an effect on the productivity of GOS is the enzyme inhibition because of the produced monosaccharides, glucose, and galactose, also termed as product inhibition. Figure 2 shows the enzymatic reaction to produce GOS from lactose. However, the inhibition differs on the source of enzyme. It had been seen that β -galactosidase extracted from *Kluyveromyces lactis* is more prone to galactose inhibition compared to glucose (Chockchaisawasdee et al. 2005). Galactose inhibition takes place in a competitive way (Gosling et al. 2010), while glucose inhibits in both competitive and uncompetitive way (Gosling et al. 2010). One of the critically acclaimed GOS products that is obtained in the market with substantial demand is Vivinal GOS syrup. The reason behind its syrupy form is its low solubility in water and is practically insoluble in ethanol as GOS is a mixture of different



Galacto-oligosaccharides, Fig. 2 Reaction schematics for GOS production from lactose with enzymatic route

carbohydrate polymers having different molecular weight with differential solubility. It had been seen that after producing GOS from lactose through enzymatic route, it can be separated out from the mixture of unreacted lactose, glucose, and galactose with 90 % (v/v) ethanol addition at 40 °C temperature (Sen et al. 2011).

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Galvanic Replication

► [Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices](#)

Gas Diffusion Electrode (GDE)

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The membrane electrode assembly is an assembly of an electrolyte and a catalyst layer either side of the electrolyte which is then hot pressed between two gas diffusion layers to form a single component. Each side of the membrane then forms an electrode, often called a gas diffusion electrode (GDE) which is a combination of the catalyst layer and the gas diffusion layer.

In the early days, sintered electrodes were used which were thick and quite heavy, but since 1970, bonding methods are employed to produce

electrodes with polytetrafluoroethylene (PTFE) materials. Electrodes made up of PTFEs are stable and have hydrophilic and hydrophobic properties which are important for providing required conductivity for electron transport and for removal of produced water. For acidic electrolytes such as the PEM, the principle catalyst used is platinum. An important feature for MEA preparation and manufacture is to ensure that there is good integration between the three components, the electrolyte, catalyst layer, and gas diffusion layer. These components must be interconnected to form a triphase point (TPP) which is critical for electrochemical reactions to take place and subsequently the performance of the fuel cell. The electrolyte and the Pt catalyst must be in contact to allow the transfer of the mobile ion to/from the reaction surface. The Pt catalyst must also have good contact with the GDL which will allow the transfer of electrons to and from the reaction site. Finally, the porous GDL must allow excellent diffusion of the reactant species to the reaction site while it facilitates product species away from the site. Careful optimization of the GDE is therefore essential as it is directly linked to the performance of the fuel cell and also the utilization of the Pt catalyst as the Pt catalyst that does not fulfill the triphase point criteria will not participate in electrochemical reactions.

Gas Diffusion Layer (GDL)

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The GDL is important part of polymer electrolyte membrane PEM and direct methanol DM fuel cell. There are two gas diffusion layers

(cathode and anode sides) which as the name suggests diffuse reactant gases to the catalyst layer (of the electrolyte membrane). Other main functions include removing excess water and heat away from the catalyst layer for the smooth operation and preventing flooding. GDL is capable of retaining some water to ensure good conductivity throughout the membrane. It provides mechanical strength and support to the catalyst and membrane. GDL is electrically conductive; it also provides pathway for current collection. Thus, the main requirements of GDL are permeability of gases and water, conductivity, and mechanical strength. Due to these requirements, GDL is most commonly made up of carbon fiber-based products, i.e., cloth and carbon paper. As carbon cloth is thicker than carbon paper, it has certain advantages compared to carbon paper. Carbon cloth is made by weaving carbon fibers and therefore more flexible and stronger than carbon paper-based GDL layers. New generation GDL material combining the benefits of carbon cloth and paper is also being investigated by some researchers.

Due to different considerations for a GDL, many factors such as type of carbon used, pore formation, and thickness play an important role in the fabrication of GDL for a particular application. In most cases GDL consists of two layers: macroporous diffusion medium (DM) and microporous layer (MPL) typically 200–400 μm thick. DM has pore size ranging from 10 to 30 μm , and MPL has pore size of 0.05–5 μm and is purposely made hydrophobic by treating with small amount of Teflon or PTFE (5–10 wt.%). The small pore size creates a capillary pressure gradient across the membrane for effective removal of water away from the reaction sites.

Gas Permeability

► Permeability

Gas Permeance

► Permeance

Gas Permeation Unit (GPU)

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The intrinsic permeation property of a gas through a membrane is characterized by the *permeability coefficient* P of a gas A, P_A . *Barrer* was early introduced as a practical unit for this property and made it easy to compare the suitability of materials to be used for membrane gas separation. *Barrer* is also defined below.

Permeance is directly related to the thickness, l , of the membrane and as such defined as pressure-normalized steady-state flux, P/l . The permeance will characterize the gas transport through the membrane. Permeance is an important parameter when comparing the separation suitability of membranes for mixed gases. A practical unit often used is *GPU* (*gas permeation unit*) (see below).

Permeability:

$$\begin{aligned} 1 \text{ Barrer} &= 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1} \\ &= 1.33 \times 10^{14} \text{ m}^3(\text{STP}) \text{ m m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1} \\ &= 2.99 \times 10^{15} \text{ kmol m m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1} \end{aligned}$$

Permeance:

$$\begin{aligned} 1 \text{ GPU} &= 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1} \\ &= 7.6 \times 10^{-9} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1} \\ &= 3.35 \times 10^{-3} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1} \end{aligned}$$

(For conversions on membrane key parameters, please refer to: Table according to Journal of Membrane Science.)

Gas Permeation: Permeability, Permeance, and Separation Factor

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General

Detailed information on the topic of gas separation with membranes can be found in numerous textbooks and chapters in membrane handbooks – only four book references are mentioned here: *Basic Principles of Membrane Technology* (Mulder 1996), *Materials Science of Membranes for Gas and Vapor Separation* (Yampolskii et al. 2006), *Handbook of Membrane Separations* (Pabby et al. 2015), and *Membrane Technology and Applications* (Baker 2012).

The use of membranes for gas applications dates back to the 1980s when the first commercial application was made economically feasible by the work of Henis and Tripodi (1980), for hydrogen recovery from a gas stream at a petrochemical plant. The first membranes developed were usually polysulfone or cellulose acetate, while today's commercial gas membranes include various types of polymers, especially should be mentioned polyimides. The research internationally on membrane materials for gas applications is comprehensive; however, relatively few new materials have made it to commercial applications. The potential for the industrial use of membranes in gas separation and purification is huge. The technology is environmentally friendly and a great technology for process intensification. The commercial processes where membranes for gas separation are applied today are mainly H₂ from gas streams, O₂/N₂, CO₂/H₂, CH₄/CO₂ (natural gas and biogas), vapor/gas separations, dehydration of air, and vapor/vapor separations. The potential for other gas separations is many.

There are basically two main categories of membrane gas separation: the synthetic materials

(polymers) and the inorganic materials (carbon, ceramic, metal (palladium especially)). The gas separation will take place according to different transport mechanisms depending on the intrinsic membrane material properties and the physical properties of the gases.

Dense polymeric materials may be in their glassy or rubbery state depending on their glass temperature (T_g) and the operating conditions. Separation is basically according to solution-diffusion. In its glassy state, the diffusion of the gas component will be governing the selectivity between the gases, while in its rubbery state, the solution of the gas in the membrane material will be of major importance. As a rule of thumb, the selectivity will be high and permeation low in a glassy, dense membrane, while selectivity will be low and permeation high in a rubbery material. The properties of the gas will also be important for the gas separation: an inert gas (like H₂, N₂, also CH₄) has very low critical temperature and will not easily dissolve in the material. Hydrocarbons, however, and nonideal gases like CO₂ have relatively high critical temperatures and will easily dissolve in the material and hence also swell the membrane. This will naturally affect the separation, and the selectivity will go down. It is thus of major importance to evaluate the suitability of the material for the separation of the gas pair in question and also with respect to process conditions for the potential application. The basic equations for gas separation are

$$J_i = -D_{ij} \frac{dc_i}{dx} \quad (1)$$

where J_i is the flux of component i [mol/(m²s)], D_{ij} is the diffusion coefficient [m²/s], and dc_i/dx is the concentration gradient for component i over the length x [mol/(m³·m)] (Fick's law). This converts to

$$J_i = \frac{P_i}{l} (\Delta p_i) \text{ when considering gases} \quad (2)$$

where $P_i = D \cdot S$ is the permeability of i (D is diffusion $\times S$ solution) and P_i/l is the permeance

of i through the membrane, while Δp_i is the partial pressure driving force of component i .

The “ideal” separation factor, α^* (Eq. 3), may be expressed by the ratio of the pure gas permeabilities for the individual components i and j :

$$\alpha_{ij}^* = \frac{P_i}{P_j} \quad (3)$$

The separation factor for gases in mixture α_{ij} (Eq. 4) is expressed by the mole fractions of the components in the feed (x) and the permeate (y), respectively:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j} \quad (4)$$

As a general rule, the driving force of membrane gas separation is the difference in partial pressures (concentrations) between feed and permeate side. It is however more correct to say that the driving force is the difference in chemical potential thereby including the effect of temperature. (An additional driving force may be an electric potential or a carrier effect for certain types of membranes.) New membrane materials may combine different transport mechanisms and thereby increase the flux and selectivities.

Transport through a dense polymer may be considered as an activated process which can be represented by an Arrhenius type of equation. This implies that temperature may have a large influence on the transport rate. Equations 5 and 6 express the temperature dependence of the diffusion coefficient and solubility coefficient in the Eq. $P = D \times S$:

$$D = D_0 \exp(-E_d/RT) \quad (5)$$

$$S = S_0 \exp(-DH_s/RT) \quad (6)$$

where E_d is the activation energy for diffusion, ΔH_s is the heat of solution, and D_0 and S_0 are temperature-independent constants.

Several ways are investigated in trying to increase the separation factor. New polymeric membrane materials may be functionalized to

promote the permeation of one of the components, or the membrane may be a mixed matrix, i.e., with (nano)particles dispersed in the polymeric phase. The functionalization will then add an extra driving force to the permeation, and an extra term will be added to Eq. 2, as shown in Eq. 7 below. The characteristic of facilitated or carrier-mediated transport is the occurrence of a reversible chemical reaction or complexation process in combination with a diffusion process. The total flux of a permeant A will thus be the sum of both the Fickian diffusion (Eq. 1) and the carrier-mediated diffusion as illustrated below. The driving force in both terms is here expressed as concentrations, c :

$$J_A = \frac{D_A}{l} (c_{A,0} - c_{A,l}) + \frac{D_{AC}}{l} (c_{AC,0} - c_{AC,l}) \quad (7)$$

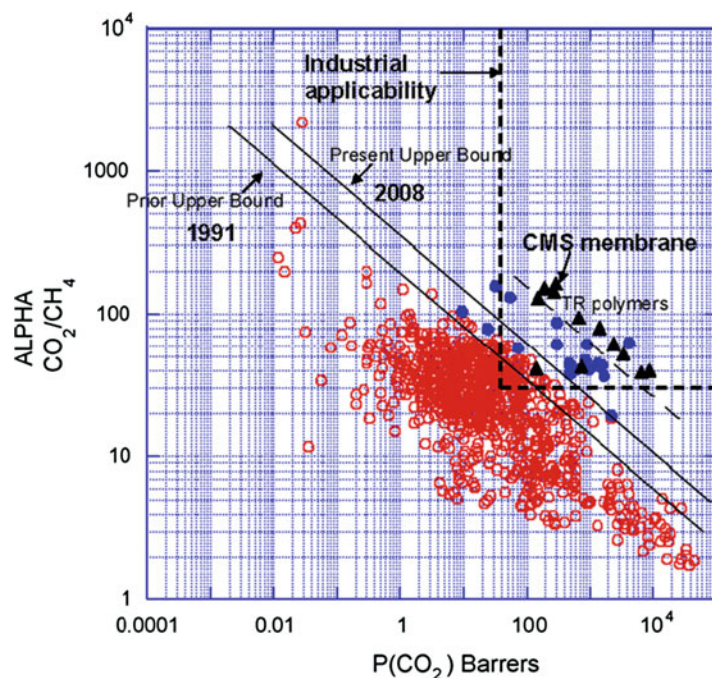
where the first term on the right-hand side of the equation is the Fickian diffusion (D_A) and the second term represents the carrier-mediated diffusion (D_{AC}). l is the thickness of the membrane.

The other main gas separation mechanism is the molecular sieving. In this group, one typically has the carbon membranes and other inorganic membranes. Molecular sieving depends on the pore diameter compared to the molecular diameter and will usually take place when diameter, $d_p < 5 \text{ \AA}$. If the pore is larger, there is the possibility of selective surface flow ($5 \text{ \AA} < d_p < 12 \text{ \AA}$) where the critical temperature of the gases will influence the separation. Too large pores may give Knudsen diffusion ($d_p > 20 \text{ \AA}$) which is not wanted.

The need for optimized membrane separation properties for specific gas mixtures has kicked off an explosive development with respect to tailor-made polymeric membrane. The first goal for most membrane material development is to document performance in the economically interesting region as shown in now so well-known Robeson plot for polymeric membranes, having an upper-bound trade-off between gas permeability and selectivity (Robeson 2008) – shown here in Fig. 1. The gas separation will, however, depend

**Gas Permeation:
Permeability,
Permeance,
and Separation Factor,**

Fig. 1 Selectivity for the gas pair CO_2/CH_4 as function of CO_2 permeability and the Robeson plot (squares for CMS (carbon) membranes, solid circles for TR (thermally rearranged) polymers, triangles for FSC (fixed-site-carrier) membranes, and solid diamonds for PIMs) (Adapted from Robeson 2008)



both on efficient separation of the gases in mixture and the relevant process conditions and, last but not least, also durability of the material over time.

Membrane gas separation is complex and challenging, and for a full understanding of the topic, competence on material technology and processes is needed. The *four books* listed here are excellent references on the topic.

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Gas Separation

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Gas separation is a widely used technique in which the objective is the separation of one or more gases from a mixture. It is becoming crucial for several industrial processes such as the treatment of fumes from coal-fired plants, in particular, aiming for the removal of CO_2 to reduce the greenhouse effect. Growing interest is also given to other applications such as the separation and purification of commercially important gases such as H_2 , CH_4 , and O_2 from natural gas. The most common methods to perform gas separation are:

1. Separation with solvent/sorbents
2. Separation by cryogenic distillation
3. Separation with membranes

Separation with Solvent/Sorbents

The separation with solvent/sorbents is based on the affinity of the gas toward a specific sorbent such as zeolites, alumina, or activated carbon or a solvent, for instance, MEA (methanolamine). The most illustrative example of this technology is represented by the pressure swing adsorption (PSA) method. The separation occurs when the gas mixture comes in contact with the sorbent/solvent in a vessel which is then pressurized. The gas with the highest affinity for the adsorbent is “trapped,” whereas the others pass through the system. The regeneration of the vessel is carried out by returning it to atmospheric pressure or by increasing the temperature, with release of the “trapped” gas. The main advantage of this technique is the high purity of the separated gas; the disadvantage consists in the high energy required

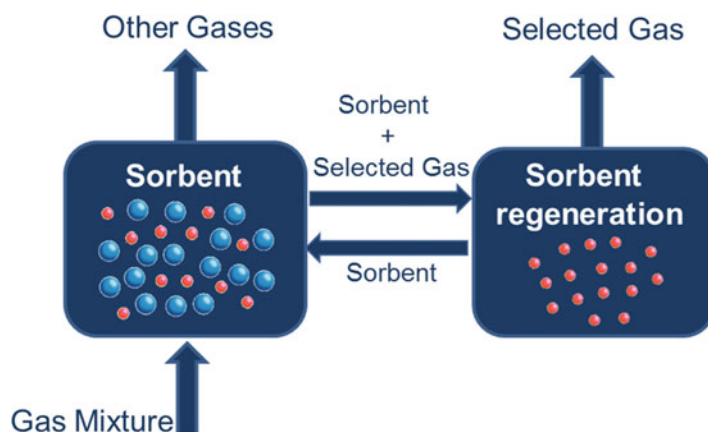
for running the system, especially for the regeneration of the vessel (Fig. 1).

Separation by Cryogenic Distillation

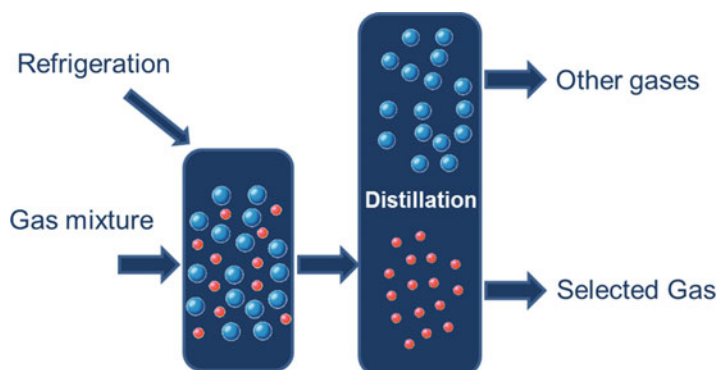
Cryogenic distillation is based on the fact that in a mixture of gases, they all have different boiling points and they could be separated by increasing/decreasing the temperature and pressure of the system in which they are stored, so that they can be divided into their single components. The gas mixture is cooled down to a low temperature (typically $< -50\text{ }^{\circ}\text{C}$). Once in the liquid form, the components of the gas can be directed in a distillation column, and through a series of compression, cooling, and expansion steps, they can be distributed to different channels, depending on their boiling points (Fig. 2).

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Gas Separation,
Fig. 1 Schematic representation of pressure swing adsorption method (PSA)



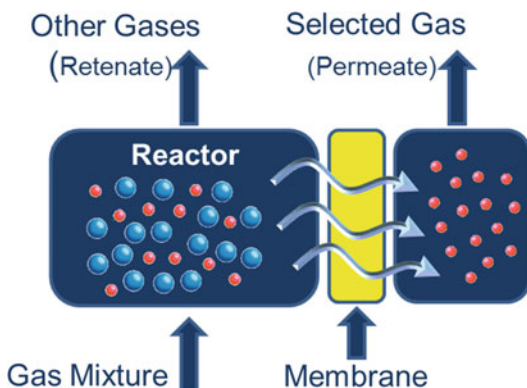
Gas Separation,
Fig. 2 Schematic representation of cryogenic distillation method



It is a widely used technique for streams that already have a high concentration of desired gas (typically >90 %), but it is not very appropriate for more dilute gas streams.

The main advantage of the cryogenic gas separation is that it enables direct production of liquid gas, which is often very useful for certain transport options, such as transport by ship.

A major disadvantage is connected with the high amount of energy required for the refrigeration especially for dilute gas streams.



Gas Separation, Fig. 3 Schematic representation of membranes for gas separation

Separation with Membranes

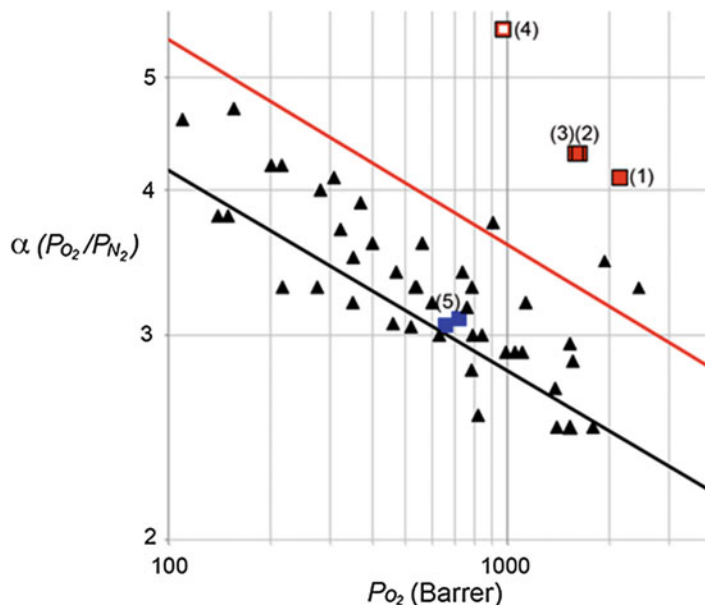
Separation of gases with membranes relies on the different affinities of one or more gases toward the membrane material, causing one gas to permeate faster (or slower) than others. It is one of the fastest growing field for gas separation techniques, especially due to the high variety of materials which the membrane could be composed of, including microporous organic polymers, zeolites, ceramic, and metal-containing materials (for a more in-depth reading, see Yampolskii and Freeman (Yampolskii et al. 2010)).

The gas mixture is directed into a vessel and put in contact to the membrane material which is at the interface with another vessel (Fig. 3). The mixture is allowed to diffuse into the second vessel under a pressure gradient which promotes the mass transport through the membrane separating the retentate (slower gas) from the permeate (faster gas).

The use of membranes for gas separation offers several benefits, probably the most valuable is the high cost efficiency (both for the mechanical simplicity of the system and for low-energy regeneration). In fact, they do not require thermal regeneration, a phase change, or active moving parts in their operation.

Gas Separation,

Fig. 4 An example of Robeson plot, in this case O_2/N_2 (Carta et al. 2013). The black line represents the 1991 (Robeson 1991) upper bound, whereas the red line is the current (2008) upper bound (Robeson 2008)



Probably the greatest limitation of membranes for gas separation is derived from their trade-off relationship between permeability and selectivity for a required gas component. This means that high permeable membranes have low selectivity, requiring several run for a good separation, and highly selective membranes have low permeability, meaning long operational times. This trade-off was well addressed by Robeson in two well-known articles (Robeson 1991, 2008) in which he studied the gas separation performance of several membrane-forming materials in terms of permeability of a particular species (P_A) and selectivity toward one component of a gas pair ($\alpha_{A/B} = P_A/P_B$), organizing the data in double logarithmic plots for a series of commercially selected important gas pairs such as H_2/CH_4 , H_2/CO_2 , and O_2/N_2 . He confirmed that highly selective membranes generally exhibit low permeability and vice versa. The most important outcome of this study is represented by the so-called Robeson upper bound, an empirical line which is drawn for every gas pair plot that is meant to define how good a material for gas separation is. In Fig. 4, there is a typical example (Carta et al. 2013) in which the red line represents the 2008 upper bound for the gas pair O_2/N_2 . Supposedly, if we plot the selectivity $\alpha_{A/B}$ versus permeability P_A for a new membrane and the data point fall close or go over the upper bound, it is widely accepted that the material has an excellent compromise between P (rate of separation) and α (goodness of separation).

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Gas Separation by Membrane Operations

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The separation of mixtures of gases and vapors is required in manufacturing processes across various industries. In the last years, membrane systems are gaining a larger acceptance in industry for gas separation and are recognized as a cost-efficient separation able to compete with consolidated processes such as pressure swing absorption and cryogenic distillation (Bernardo et al. 2009; Sanders et al. 2013). Membrane processes have several advantages over conventional separation techniques (e.g., distillation, extraction, absorption, and adsorption), including modularity and compactness, operational flexibility, and no need for energy-intensive phase changes or potentially expensive adsorbents and/or difficult to handle solvents. The features of membrane operations allow implementing the process intensification strategy in different production cycles. Their versatility represents a decisive factor to impose membrane processes in most gas separation fields.

The first membrane units were installed in ammonia plants for the separation of hydrogen from nitrogen more than 30 years ago. Today, the production of nitrogen from air is the largest application of membrane systems, owing to the demand for nitrogen to inert fuel tanks, also aboard aircrafts, and for blanketing chemical and liquefied gas shipments. Membrane systems are also applied to enrich oxygen for medical uses, for hydrogen recovery and purification in refineries, for air and gas dehydration, and for ratio adjustment of gas mixtures. Natural gas processing represents an important emerging application field (Baker and Lokhandwala 2008). The relatively low volume flow and the relatively high inlet carbon dioxide content are strong drivers for the

implementation of the membrane technology in the biogas upgrading that it is at a developing stage (Makaruk et al. 2010). The challenging olefin/paraffin separation, not yet commercial, is attracting a lot of interest from the scientific community (Rungta et al. 2013).

Membrane separation allows recovering and recycling valuable compounds, such as hydrogen and light hydrocarbons (ethylene, propylene, and LPG), present in different off-gas streams (Baker et al. 1998). Polymeric membranes, cheap and with an easy processability, are typically used in the commercially available membrane system for gas separation (Yampolskii 2012). Commercial modules employ composite membranes (Pinnau et al. 1988), mainly in the form of compact hollow fibers. These membranes typically operate the separation based on a solution-diffusion transport mechanism: sorption of the permeant into the membrane, permeation by diffusion through the membrane, and desorption at the low-pressure side of the membrane.

The experimentally observed upper bound, based on various polymeric membranes, was reported by Robeson in 1991 and then updated in 2008 (Robeson 1991, 2008), thanks to the efforts to improve the gas separation performance of ultrahigh free volume and perfluoropolymers.

Glassy polymers are chosen for their size-selective behavior (e.g., in O_2/N_2 or H_2 separations). However, when applied to mixtures and/or at high gas activities, these materials are prone to plasticization, which causes swelling of the polymer matrix and results in a higher permeability coupled with a loss of selectivity. Strategies to overcome plasticization include thermal curing and chemical cross-linking, which reduce the polymer free volume (Wind et al. 2002). The addition of nanofillers to a polymer matrix represents an interesting solution to overcome the trade-off of the polymeric membranes and the inherent brittleness issues of inorganic membranes (Goh et al. 2011).

Rubbery polymers, instead, present a solubility-controlled permeation and preferentially allow the permeation of large gas or vapor molecules in a gaseous mixture containing also smaller molecules (Grinevich et al. 2011). Their permeability, much higher than in conventional

glassy polymers, increases with the critical volume of the penetrant (Matteucci et al. 2006). These materials are applied to the separation of organic vapors from non-condensable gases, treating petrochemical vent and process streams to recover valuable feedstocks (Baker 1999).

An interesting new concept is the use of water-swollen thin film composite membranes for biogas purification, taking advantage of the large difference in solubility in water to become selective for CO_2 (Kárászová et al. 2012).

Facilitated transport membranes contain carrier agents that can react reversibly with the target gas component. Therefore, the reaction in the membrane creates another transport mechanism, in addition to the simple solution-diffusion mechanism (Huang et al. 2008). However, carrier poisoning and short life span of the polymeric membranes are typically reported (Rungta et al. 2013). Ionic liquids were considered as additives for facilitated transport membranes. Indeed, their negligible vapor pressure avoids solvent losses by evaporation, providing stability to the metallic cation dissolved inside, and acting as a medium for facilitated transport with mobile carrier (Fallanza et al. 2013). Ionic liquid gel membranes based on conventional polymers (Jansen et al. 2011) or on polymer ionic liquids (Bara et al. 2008) were proposed to increase the stability compared to supported liquid membranes.

The key for new applications of membranes in challenging and harsh environments (e.g., petrochemistry) is the development of new tough, high-performance materials. In the field of inorganic membranes, metal organic frameworks were recently considered for preparing membranes to be applied to the olefin/paraffin separation (Bux et al. 2011) or as additive to a polymer matrix (Bushell et al. 2013).

High free volume polymers have been investigated as gas separation membranes, combining their ease of processing and mechanical stability with the potential to surpass the polymeric upper bound for different gas pairs (Budd and McKeown 2010). Novel PIMs, characterized by a significant shape persistence, were developed, showing interesting performance for the O_2/N_2 separation (Carta et al. 2013).

Properly designed hybrid processes, combining a membrane system with a conventional one (e.g., PSA or absorption), represent technically and economically viable solutions, able to reduce energy consumption and total costs (Esteves and Mota 2007).

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Gas Separation Membranes: High-Temperature Glass Joining and Sealing

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Gas separation membranes such as ceramic mixed ionic-electronic conducting (MIEC) membranes are able to transport oxygen or protons through their crystal structure at high temperatures

(>700 °C) in the presence of a driving force (Sunarso et al. 2008). This can be accomplished by sealing the membrane to a ceramic (alumina, zirconia, or mullite) or metal tube. Since the membranes can have different geometries, such as disk or tubular, diverse seal positions are possible, which are illustrated in Fig. 1.

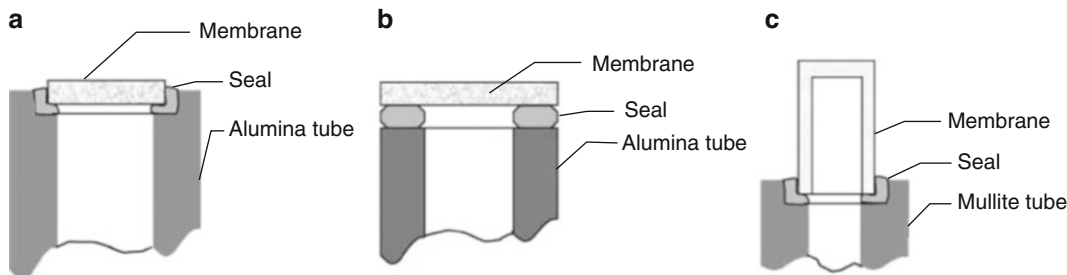
This seal must be gastight at the operating temperatures (700–1000 °C) of the membranes. However, MIEC membranes have a very high thermal expansion coefficient ($\text{CTE} > 20 \times 10^{-6}/\text{K}$) compared to the materials to which they are bonded (CTE of $8\text{--}15 \times 10^{-6}/\text{K}$). As such, at the operating temperatures of the membranes, there is a big thermal expansion mismatch between the materials, which can cause failure of the joint. Therefore, to achieve a gastight joint, there must be a good wettability of the seal on the membrane and the support, and the seal must have a suitable viscosity and coefficient of thermal expansion (CTE) in the required temperature range. Once a seal is obtained, it must be thermal, chemical, and mechanical stable during the operation of the membrane to maintain the gastight joint.

There are different types of sealing methods for joining ceramic gas separation membranes at high temperature: metal-based seals, compressive seals, and glass-based seals. Metal-based seals can be applied by active metal brazing or reactive (air) brazing, and they will form a compliant seal. However, noble metals (Au, Pt) are expensive, while seals obtained with braze alloys, mostly Ag or Cu based, can suffer from cracks and delamination due to the CTE mismatch. Compressive seals are formed by using a deformable material, typically mica based, under a compressive load. This load is

difficult to apply on the ceramic membranes, and the seals are generally of lower quality than other types of seals. The last group of seals, the glass-based ones, form rigidly bonded seals by forming chemical bonds with the other materials and providing a hermetic joint. Furthermore, the properties of the glass or glass-ceramic seal can be tailored by changing the composition of the glass, and they are less expensive than noble metals (Qi et al. 2001; Mahapatra and Lu 2010; Vivet et al. 2011). As such, glass-based seals are very promising for high-temperature sealing of membranes.

A glass seal can consist of different constituents such as a network former (SiO_2 or B_2O_3), a network modifier (Li_2O , Na_2O , K_2O , BaO , SrO , CaO , MgO), an intermediate (mostly Al_2O_3), and an additive (Fig. 2). The first two constituents will have the most influence on the CTE, the glass transition temperature T_g , and the softening temperature T_s of the glass. These are important characteristics since the CTE must match as much as possible with the joining materials, T_g must be below the operating temperature of the seal otherwise the seal becomes brittle, and T_s must be higher than the operating temperature to avoid excessive flow of the seal.

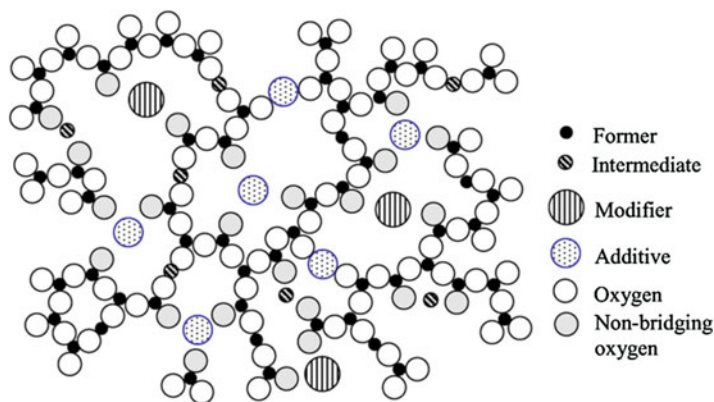
An example of a glass-ceramic composite seal which can be used for high-temperature sealing of ceramic membranes for gas separation is based on Pyrex 7740 (SiO_2 80.6 wt%, B_2O_3 13 wt%, Na_2O 4 wt%, Al_2O_3 2.3 wt%, and K_2O 0.1 wt%), membrane material powder, and NaAlO_2 or B_2O_3 (Qi et al. 2001). This glass-ceramic composite is able to form a gastight seal between ceramic membranes such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.95}\text{Tb}_{0.05}\text{O}_3$ and alumina or mullite in the temperature range of 600–950 °C.



Gas Separation Membranes: High-Temperature Glass Joining and Sealing, Fig. 1 Schematic illustration of high-temperature seal positions to fix a disk or

tubular membrane to an alumina or a mullite tube for oxygen separation (Qi et al. 2001)

Gas Separation Membranes:
High-Temperature Glass Joining and Sealing,
Fig. 2 Schematic illustration of a glass network structure (Mahapatra and Lu 2010)



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Gas/Vapor Transport

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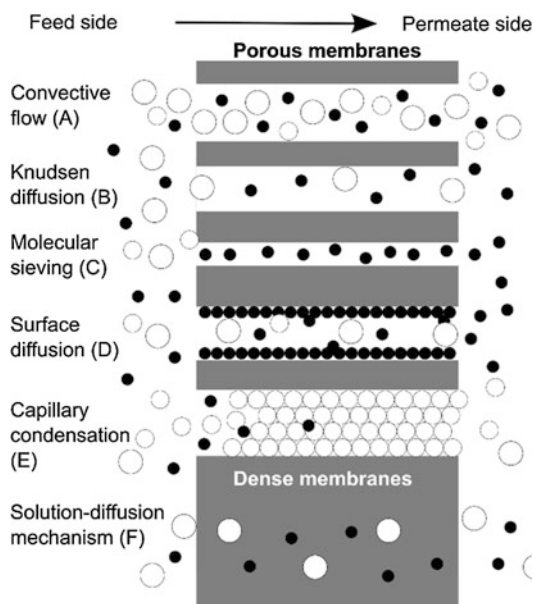
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General Introduction

Transport of gases and vapors in membranes depends first of all on their micro- and macroscopic structure. There is a fundamental difference between dense membranes, where transport takes place through the material of the membrane

itself, and porous membranes, where the transport takes place through the open space of the pores in the membrane. In the latter, different transport modes exist, depending on the size of the pores and on the interaction of the gases and vapors with the membrane material and with themselves. The most representative examples of transport mechanisms are shown in Fig. 1.

- (A) In large pores, convective or viscous flow occurs. Such membranes find application as filters to remove particulate matter from gas and liquid streams, but they are not able to separate gases, which move as a homogeneous mixture through the pores.
- (B) If the average pore diameter is smaller than the mean free path between the molecules in the gas mixture at the given pressure, so-called Knudsen diffusion takes place (Knudsen 1909; Datta et al. 1992). In this case, the transport rate is inversely proportional to the square root of the molecular weight of the gas species and the selectivity is only a function of their molecular weight ratios.
- (C) For even smaller pores, where the size of the pores is in the range of the size of the gas molecules themselves, molecular sieving can occur. Molecules that are larger than the pore size are completely excluded, and only smaller molecules may diffuse through the pores of the membrane. Such membranes can have very high selectivities, in the case of very narrow pore size distributions. Typical examples are carbon membranes (Vu et al. 2001) or zeolite



Gas/Vapor Transport, Fig. 1 Schematic representation of different transport mechanisms in porous and dense membranes

membranes (Caro and Noack 2008; Rangnekar et al. 2015). Also dense polymer membranes, when they have a combination of very high free volume and high stiffness of the polymer chains, may exhibit behavior that comes close to molecular sieving (Carta et al. 2013).

- (D) In the case of strong interaction of the membrane material with the permeating species or in case of readily condensable species, the latter condenses on the pore wall. In this case, what is the most permeable species depends on various factors, including the molecular dimensions of the permeating species of the mixture and on the remaining aperture of the pores, as well as the mobility of the condensed species on the pore surface.
- (E) In the extreme situation of the previous, capillary condensation takes place and the whole pore is filled with the condensed liquid. The selectivity of these membranes for gas mixtures may be completely different from the ideal selectivity for single gases. Based on the Knudsen diffusion mechanism, small molecules would always be much more permeable

than larger molecules. However, if the larger molecules condense inside the pore, the condensed phase obstructs the permeation of smaller molecules. Thus, the mixed gas selectivity may be opposite to the ideal selectivity.

- (F) In dense membranes, the molecules move through the bulk of the membrane material itself, or more precisely through its free volume. The rest of this chapter will focus mostly on the transport in dense membranes because of their relevance for gas separation applications.

Gas/Vapor Transport in Dense Membranes

Fick's Law of Diffusion

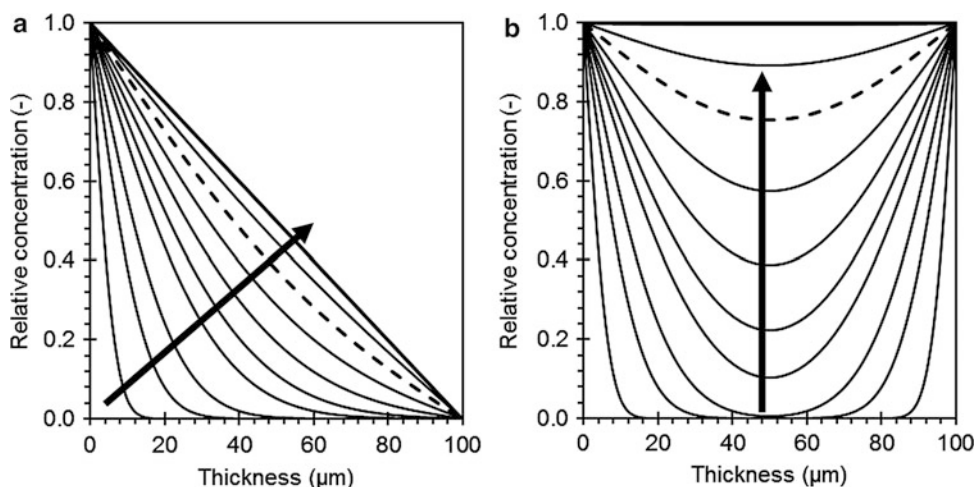
The penetrant flow, J , through a nonporous membrane can be described by Fick's first law of diffusion (Fick 1855), derived analogically to Fourier's law for the description of heat transfer.

$$J_i = -D_i \frac{dc_i}{dx} \quad (1)$$

where D is the diffusion coefficient and dc/dx the concentration gradient. The concentration in nonstationary conditions depends not only on the position in the continuous phase but also on time. Assuming one-dimensional diffusion, the transport behavior can be described by Fick's second law of diffusion:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \quad (2)$$

Both equations assume that the diffusion coefficient is independent on concentration, which is true at low penetrant activity. Figure 2 describes the gas concentration profile at different times, for a previously evacuated polymer membrane after single-sided and double-sided exposure to a gas, based on Eq. 2 (Crank 1975). These profiles correspond to those in a typical permeation and sorption experiment, respectively.



Gas/Vapor Transport, Fig. 2 Concentration profiles in a flat sheet membrane (100 μm) calculated by Eq. 2, for $D = 10^{-12} \text{ m}^2 \text{ s}^{-1}$ (Crank 1975) in the case of: (a) ideal time lag permeation experiment (Relative feed concentration = 1, permeate concentration = 0); (b) ideal

sorption experiment (Relative feed concentration = 1) Arrows represent the increasing time during the experiment. Dashed lines represent the concentration profile in time equal to permeation time lag (see below)

The Solution-Diffusion Mechanism

The transport of gases and vapors in dense polymer membranes is governed by the solution-diffusion model (Wijmans and Baker 1995, 2006). The driving force of this process in dense membranes is the partial pressure gradient of the permeating species across the membrane, or more correctly its chemical potential gradient. The process consists of three steps: first, the gas is absorbed by the membrane at the polymer/gas interface on the feed side, then it diffuses across the polymer bulk, and finally it desorbs from the membrane at the permeate side. The permeability coefficient, P , is the product of the diffusion coefficient, D , and the solubility coefficient, S :

$$P = D \cdot S \quad (3)$$

where S is defined as the ratio of the equilibrium gas concentration, C , and the gas pressure, p :

$$S = C/p \quad (4)$$

The selectivity $\alpha_{A/B}$ of two species A and B is defined as the ratio of the two individual permeability coefficients and this can be decomposed into a diffusion selectivity term and a solubility selectivity term:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \cdot \frac{S_A}{S_B} \quad (5)$$

In ideal systems, such as for the transport of light gases in rubbers, P , D , and S are constants, but this is rather an exception and in many cases D and S depend on the concentration of the permeating species in the membrane and thus on the gas pressure. Numerous correlations have been proposed, relating the gas and vapor transport properties of polymeric membranes to the molecular properties of the penetrating species and to the chemical and physical properties of the polymer matrix, and they can be found in an excellent review (Matteucci et al. 2006).

In phenomenological terms, the membrane productivity is expressed by means of its permeance, defined as an amount of permeate per unit membrane area, time, and driving force. A commonly used unit is the gas permeation unit, GPU:

$$\begin{aligned} 1 \text{ GPU} &= 10^{-6} \frac{\text{cm}^3_{\text{STP}}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \\ &= 2.70 \cdot 10^{-9} \frac{\text{m}^3_{\text{STP}}}{\text{m}^2 \cdot \text{h} \cdot \text{bar}} \end{aligned} \quad (6)$$

The permeance is a property of the membrane and depends on its effective thickness. The permeability coefficient is an intrinsic property of the material. The most commonly used unit to describe the permeability coefficient is the Barrer:

$$1 \text{ Barrer} = 10^{-10} \frac{\text{cm}_{\text{STP}}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \quad (7)$$

Diffusion is an activated process and solubility is a thermodynamic property. The temperature dependence of diffusivity and solubility can therefore be described by the following Arrhenius and van't Hoff relationships, respectively (Van Amerongen 1946; Costello and Koros 1992).

$$D = D_0 \cdot e^{-E_D/RT} \quad (8)$$

$$S = S_0 \cdot e^{-\Delta H_s/RT} \quad (9)$$

where ΔH_s is the enthalpy of sorption of the penetrant in the polymer, E_D activation energy of diffusion, and D_0 and S_0 are the preexponential factors.

Assuming solution-diffusion model (Eq. 3), temperature dependency of permeability is:

$$P = P_0 \cdot e^{-E_P/RT} \quad (10)$$

where P_0 is preexponential factor and E_P activation energy of permeation which is equal to:

$$E_P = \Delta H_s + E_D \quad (11)$$

As a temperature-activated process, diffusion usually accelerates with temperature. Dissolution of the gas can be considered as a two-step process of condensation of the gas phase, followed by mixing with the polymer matrix. For light gases, the solubility therefore increases with increasing temperature, because the negative enthalpy of condensation is negligible with respect to the positive enthalpy of mixing. On the other hand, enthalpy of sorption of more condensable gases and vapors is negative due to the high negative enthalpy of condensation and the solubility decreases with increasing temperature.

Temperature dependency of diffusivity is usually stronger than that of solubility, and therefore the permeability usually increases with increasing temperature (Ghosal and Freeman 1994).

Gas/Gas, Gas/Vapor, and Vapor/Vapor Separation

The most important industrial applications of gas and vapor separations vary from (A) gas/gas separations to (B) gas/vapor separations, where the membrane is in contact with highly condensable species. In the extreme case of pervaporation (C), the membrane is at one side in contact with a liquid phase and at the downstream side it is in contact with a gas phase. The type of separation process dictates the possible operation conditions and the choice of the membrane materials.

- (A) For simple gas/gas separations, for instance, O_2/N_2 separation from air for pure nitrogen production or for O_2 enrichment, in principle many membrane materials can be safely used (Baker and Low 2014). The choice depends mainly on the need to achieve a high separation factor at relatively low flux or if a high flux is needed and the separation factor is less important.
- (B) For gas/vapor separations, the transport properties of the different species vary widely. Often the vapor consists of readily condensable large molecules, which have a high solubility in combination with a low diffusion coefficient, in contrast to the light gas, with a lower solubility and a high diffusion coefficient. In this case, the species in the mixture are likely to influence each other, directly via competitive sorption in the limited free volume available and indirectly via plasticization of the polymer matrix by the condensable species. The same situation occurs in gas/gas separations, where one of the two gases readily condenses at higher pressure, for instance, CO_2 . Typical examples are volatile organic compounds (VOC) removal from air (Leemann et al. 1996), or CO_2 removal from natural gas (Adewole

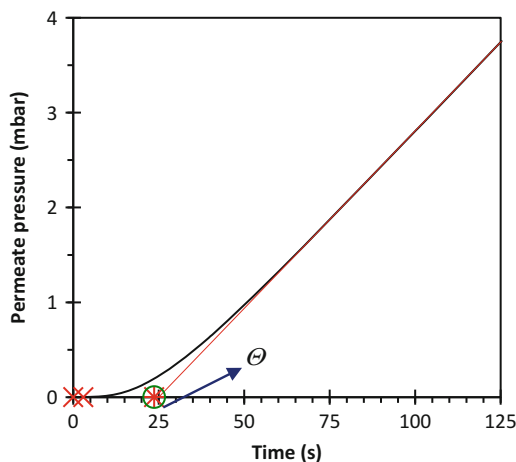
et al. 2013) or biogas, air dehydration, etc. For such separations, it may be convenient to use rubbery membranes, which are less prone to plasticization and which are solubility selective rather than diffusivity selective.

- (C) Pervaporation is the extreme case of vapor/vapor separation, with condensed vapors (=liquid mixture) at the feed side of the membrane and gaseous species at the permeate side, either by application of a vacuum or by the use of a sweeping gas (Mulder and Smolders 1991). Pervaporation is particularly advantageous in the case of azeotropic liquid mixtures, where the membrane can break the azeotrope. Typical examples of practical separations are the dehydration of alcohol with hydrophilic membranes, ethanol recovery from hydroalcoholic solutions, or VOC removal from wastewater with hydrophobic membranes. In terms of the transport properties, these membranes are often strongly affected by the swelling of the polymer by the permeating species. An exception is the alcohol dehydration with glassy perfluoropolymer membranes (Scholes et al. 2015a, b). A further complication in pervaporation with respect to gas/vapor separation is the existence of the Schroder's paradox, according to which the membrane material often behaves differently in contact with a liquid phase or in contact with the saturated vapor phase (Vallieres et al. 2006). A curiosity is that pervaporation membranes can be porous and nonselective in the dry state and become dense and selective in contact with the feed mixture (Van Der Bruggen et al. 2004, 2006).

Methods for Analysis of the Transport Parameters in Membranes

Time Lag Method for Pure Gases

The most common way to determine the basic gas transport parameters is the so-called time lag method (Crank 1975), in which the membrane is



Gas/Vapor Transport, Fig. 3 Typical permeation curve for analysis of pure gas permeability by the time lag method, with indication of time lag Θ determined via the tangent method

fully evacuated inside a closed permeation cell, and after exposure of the membrane to the gas at the feed side, the pressure at the permeate side is recorded as a function of time. For ideal systems, the concentration profile in the early stage of the experiment takes the form of Fig. 2a and the resulting permeation curve takes the form of Fig. 3, which is described by the following equation (Jansen et al. 2011):

$$p_t = p_0 + (dp/dt)_0 \cdot t + \frac{RT \cdot A \cdot l}{V_P \cdot V_m} \cdot p_f \cdot S \left(\frac{D \cdot t}{l^2} - \frac{1}{6} - ser \right) \quad (12)$$

with

$$ser = \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left(-\frac{D \cdot n^2 \cdot \pi^2 \cdot t}{l^2} \right)$$

in which p_t is the permeate pressure at time t and p_0 is the starting pressure, typically as close to zero as the vacuum pump allows. In a leak-proof instrument, the baseline slope $(dp/dt)_0$ is usually negligible for a defect-free and well-evacuated membrane. R is the universal gas constant, T the absolute temperature, A the exposed membrane area, V_P the permeate volume, V_m the molar volume of a gas at standard conditions (0 °C and 1 atm), p_f the feed pressure, and l the membrane

thickness. The permeability coefficient, P , is calculated in the regime of quasi steady state permeation, which is defined by the simplified Eq. 13, describing the tangent to the linear part of the permeation curve:

$$p_t = p_0 + (dp/dt)_0 \cdot t + \frac{RT \cdot A}{V_P \cdot V_m} \cdot \frac{p_f \cdot P}{l} (t - \Theta) \quad (13)$$

The last term is the so-called permeation time lag, Θ , which is usually determined from the intersection of the tangents before the onset of permeation and after reaching the quasi steady state:

$$\Theta = \frac{l^2}{6D} \quad (14)$$

For a membrane of known thickness, it allows the determination of the diffusion coefficient of the gas. The gas solubility coefficient, S , can then be obtained indirectly as the ratio of the permeability to the diffusion coefficient, using Eq. 3.

While the transport parameters P and D are usually obtained by using the tangents to the permeation curve, the permeation curve can also be fitted directly with Eq. 12, after expansion into a sufficient number of terms (Scheichl et al. 2005; Jansen et al. 2011). This yields the values of P , D , and S directly. An inaccurate fit in the case of a deviating curve shape is a direct indication of nonideal behavior. This happens, for instance, in the case of clustering or in the case of strong dual mode sorption (DMS) behavior.

Constant Pressure: Variable Volume Method

In this method, the pure feed gas or the feed gas mixture flows through the membrane cell in cross-flow mode and the permeate is either collected as such or it is transported by a sweeping gas to the gas analyzer. The total permeation rate can be determined directly, for instance, by a bubble flow meter or electronic flow meters, measuring the volumetric permeate flow rate, J^{Permeate} . The permeate flux, Q^{Permeate} , is the volumetric flow rate per unit area:

$$Q^{\text{Permeate}} = \frac{J^{\text{Permeate}}}{A} \quad (15)$$

When using a sweeping gas, the permeate flux can also be calculated from the known sweeping gas flow rate and the gas concentration in the permeate/sweeping gas mixture. The individual gas permeance, Π , of the i th species in a gas mixture is obtained as the ratio of its volumetric permeate flux, Q^{Permeate} , to the partial pressure difference between the feed and permeate sides:

$$\Pi_i = \frac{x_i^{\text{Permeate}} Q^{\text{Permeate}}}{x_i^{\text{Feed}} p^{\text{Feed}} - x_i^{\text{Permeate}} p^{\text{Permeate}}} \quad (16)$$

in which x_i is the volume fraction or mole fraction of the i th species, p^{Feed} and p^{Permeate} are the total feed and permeate pressures, respectively. The mixed gas selectivity of species A and B , $\alpha_{A/B}$, is then calculated as the ratio of their individual permeances:

$$\alpha_{A/B} = \frac{\Pi_A}{\Pi_B} \quad (17)$$

Sorption Analysis

Direct sorption analysis is the most reliable way to determine the solubility of the gas in the polymer matrix. Sorption can be determined volumetrically, gravimetrically, and with the pressure decay method (Keller and Staudt 2005), or by inverse gas chromatography (IGC) (Danner et al. 1998). Equilibrium sorption in polymers is one of the basic characteristics describing the interaction between a penetrant and a polymer. In all these methods, the polymer sample is placed inside the test cell and exposed to a given penetrant pressure. In gravimetric measurements, the mass uptake can be measured electromagnetically (Mamaliga et al. 2004), by a quartz crystal microbalance (QCM) (Mikkilineni et al. 1995) or McBain's quartz spiral balance (Friess et al. 2011; Vopička et al. 2013).

Since the sorption coefficient (solubility) is usually a function of pressure or activity, knowledge of the sorption isotherm shape is important. There are many different types of sorption isotherms (Rouquerolt et al. 1994) depending on

the polymer structure and the relative difference between penetrant/polymer and penetrant/penetrant interaction.

Sorption of light gases in rubbery polymers increases linearly with pressure according to Henry's law. On the other hand, vapor's sorption can be described by numerous equations such as Flory-Huggins theory (Flory 1953), Flory-Rehner (Flory and Rehner 1943a; Flory and Rehner Jr. 1943b; Izák et al. 2003), Koningsveld-Kleintjens equations (Koningsveld and Kleintjens 1971), or the ENSIC model (Favre et al. 1996).

In the case of dense glassy polymeric membranes, three models are the most often used. Permanent gases behave almost linearly, at low pressures following Henry's law. Alternatively, the dual-mode sorption model, Eq. 18, gives usually a satisfactory description of the behavior (Barrer et al. 1958). This model is a combination of Henry's law and the Langmuir sorption isotherm, assuming monolayer sorption at existing sorption sites.

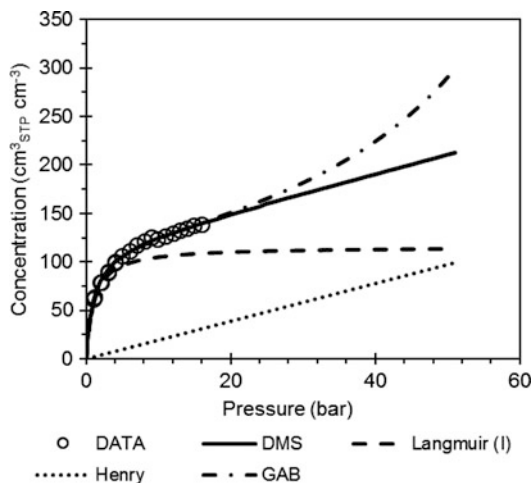
$$C = C_D + C_H = k_d \cdot p + \frac{c_h \cdot p \cdot b}{1 + b \cdot p} \quad (18)$$

where C is the gas concentration in the polymer, C_D and C_H are the Henry and Langmuir concentration contributions, respectively, k_d is the linear sorption parameter, c_h is the monolayer capacity, and b is the affinity parameter, reflecting the interaction strength between polymer and penetrant.

In the case of vapor sorption in glassy polymers, the sorption curves often have a typical S-shape and the DMS model cannot be used. In such cases, the Guggenheim, Anderson, and de Boer (GAB) model (Guggenheim 1966) gives a better description:

$$v = \frac{v_m \cdot h \cdot a \cdot f}{(1 - f \cdot a)(1 - f \cdot a + h \cdot f \cdot a)} \quad (19)$$

where v is the mass of adsorbed vapor per mass of polymer adsorbent, v_m is the capacity of the first adsorption monolayer, h defines the ratio of the adsorption strength in the first and the subsequent layers, a is the vapor activity, and f is a constant defining the deviation of the saturated vapor



Gas/Vapor Transport, Fig. 4 Gravimetric sorption isotherm of CO_2 in Amine-PIM-1 (Mason et al. 2014), extrapolated with GAB and DMS models

pressure from a chosen reference pressure. For gases, the following form of the GAB model was proposed (Vopička and Friess 2014).

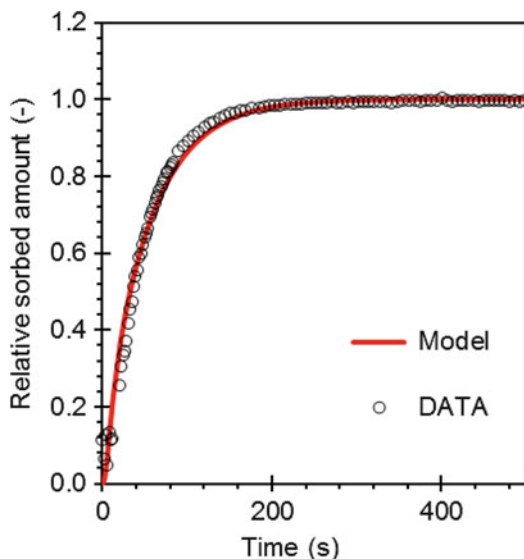
$$v = \frac{v_m \cdot h \cdot p^* \cdot p}{(p^* - p)(h \cdot p + p^* - p)} \quad (20)$$

where p^* is a pressure independent constant which has the meaning of a reference pressure. When p^* is equal to saturated vapor pressure, the model is equivalent to the BET model (Brunauer et al. 1938) (Fig. 4).

For samples with a well-defined geometry, sorption kinetics measurements allow the determination of the diffusion coefficient by equations based on Fick's second law (Crank 1975). The relative sorbed amount Q_t/Q_∞ in a flat film with thickness l is given as a function of time by the following equation:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot e^{-\frac{D \cdot (2n+1)^2 \cdot \pi^2 \cdot t}{l^2}} \quad (21)$$

The corresponding concentration-time profile in a flat membrane during a sorption experiment is shown schematically in Fig. 2b. Under real conditions, a finite time is needed to charge the gas in the sorption apparatus and a correction for the assumed step-pressure-increase is necessary



Gas/Vapor Transport, Fig. 5 Typical gravimetric sorption kinetics curve. CO₂ sorption fitted with the model proposed by Vopička (Vopička et al. 2009) in microporous Tröger's base polymer EA-TB-PIM (Carta et al. 2013) after MeOH treatment

(Vopička et al. 2009). An example of a typical sorption kinetics curve obtained with this model is shown in Fig. 5.

Modeling of Transport

With the increasing computational power of modern computers, modeling of structural (Heuchel et al. 2008) and transport properties of gases (Hofmann et al. 2000; Frentrop et al. 2015) and vapors (Giacinti Baschetti and De Angelis 2015) in polymeric membranes has gained a prominent position in membrane research. Especially in the description of the free volume distribution of membrane materials, computational methods offer a level of insight that no single experimental method can give. The transport can be studied at the atomistic level (Hofmann et al. 2000; Theodorou 2006), showing, for instance, the “hopping” mechanism of a gas molecule from one free volume element to the next, confirming the activated mechanism seen experimentally. Although there is often a large discrepancy between the calculated sorption and diffusion coefficients and the experimental values, the trends between different gas species are usually

reproduced well in the simulations (Macchione et al. 2007; Jansen et al. 2010). Whereas molecular dynamics simulations work fairly well for small molecules at low concentration, like in gas separation, models to analyze and predict the mass transport in pervaporation require different approaches (Lipnizki and Trägårdh 2001), such as the UNIQUAC model (Heintz and Stephan 1994).

Transport in Heterogeneous and Homogeneous Mixtures

The description of the transport in polymers with homogeneously or heterogeneously dispersed additives or in polymer blends is much more complex than that in neat polymers. Mixed matrix membranes are currently receiving much attention (Aroon and Ismail 2010; Rezakazemi et al. 2014) because they have the potential to combine the high permeability and selectivity of inorganic (e.g., zeolites (Miller et al. 2007)), carbonaceous (Vu et al. 2003), and organometallic filler particles (metal organic frameworks, MOFs (Bushell et al. 2013; Zornoza et al. 2013; Adatoz et al. 2015)) with the good mechanical properties of polymers. There is a large number of predictive models to describe the performance of MMMs (Vinh-Thang and Kaliaguine 2013). One of the simplest and most commonly used models to describe the transport in MMMs is the Maxwell model (Shimekit et al. 2011), valid for a low concentration of spherical particles dispersed in the continuous phase:

$$P_{eff} = \frac{P_d + 2P_c - 2\phi_d(P_d - P_c)}{P_d + 2P_c + 2\phi_d(P_d - P_c)} \quad (22)$$

where the P_{eff} is the effective permeability of the mixed matrix membrane, P_c and P_d represent the gas permeabilities in the continuous and dispersed phase, respectively, and ϕ_d is the volume fraction of the dispersed phase. Generally, the permeability of the gases through the dispersed phase depends on the overall void volume, its distribution in the filler particles, and on the channel size, which affect the free volume of the overall system.

More sophisticated models take into account also the particle shape of the dispersed phase (Cussler 1990). Such particles may have a pronounced effect in the case of high aspect ratios (Rodenas et al. 2014) due to the strong effect on the diffusion path length (Falla et al. 1996). Interestingly, also impermeable fumed silica (Merkel et al. 2002) or graphene (Althumayri et al. 2016) filler particles, with intrinsic barrier properties, can have a positive effect on the permeability of the membranes, when additional free volume is created at the polymer-particle interface.

When the dispersed phase is another polymer, in the case of immiscible polymer blends, the transport can be described by fundamentally the same equations as the mixed matrix materials (e.g., Eq. 22). Instead, for miscible polymer blends, the permeability, P_b , is reported to obey the following equation (Robeson 2010):

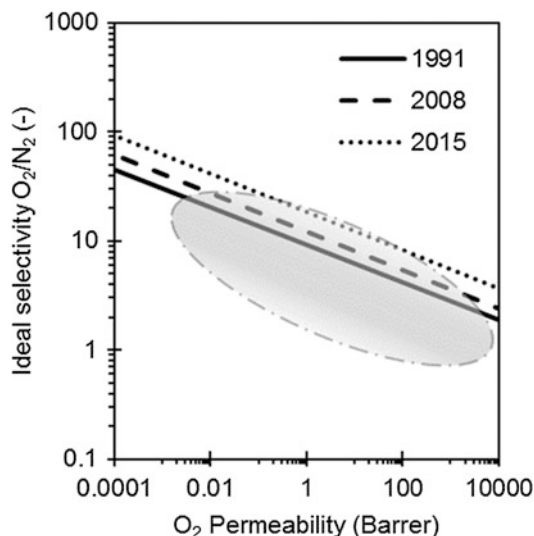
$$\ln P_b = \phi_1 \ln P_1 + \phi_2 \ln P_2 \quad (23)$$

in which ϕ_1 and ϕ_2 are the volume fractions of the two polymers, respectively, and P_1 and P_2 are their permeabilities. It shows a linear trend when the permeabilities are plotted on a logarithmic scale and deviates from linearity in the case of (partial) immiscibility of the two polymers (Jansen et al. 2013).

Overall Performance

Robeson Trade-Off Behavior

Although membrane separations may have many advantages compared to traditional separation processes such as distillation or pressure swing adsorption, a limitation is the trade-off behavior between selectivity and permeability. This trend was firstly discussed by Robeson in 1991, who suggested a linear so-called upper bound for many relevant gas pairs (Fig. 6) (Robeson 1991), which were subsequently updated and extended (Robeson et al. 1994; Robeson 2008). In 2015, a new upper bound was set for O_2/N_2 , H_2/N_2 , and H_2/CH_4 , based on mostly the development of polymers of intrinsic microporosity (Swaidan et al. 2015). Freeman discussed the basis of the



Gas/Vapor Transport, Fig. 6 O_2/N_2 1991 and 2008 upper bound curves for the selectivity versus permeability trade-off relation (Robeson 1991, 2008) with the latest upper bound suggested by Swaidan et al. (2015). The oval represents the approximate cloud of experimental data

upper bound (Freeman 1999) and concluded that a combination of high free volume and extreme rigidity of the polymer chains is needed to exceed the current upper bound (Robeson et al. 2009). This was confirmed by McKeown et al. with a novel polymer of intrinsic microporosity based on Troger's base and ethanoanthracene (Carta et al. 2013) or benzotriptycene units (Rose et al. 2015). Alentiev presented a similar approach for the trade-off in diffusion coefficient and diffusion selectivity (Alentiev and Yampolskii 2013).

Effect of Physical Aging on the Transport Properties

The global nonequilibrium state of glassy polymeric membranes tends to relax over time. This process, where no chemical changes occur, is called physical aging (Struik 1978) and affects different properties of a polymer. One of these is the free volume distribution, which, in turn, is reflected in the gas transport properties of the membrane. Physical aging therefore has a strong impact on the performance of amorphous glassy gas separation membranes (Pfromm 2006), and gas diffusion is a very sensitive method to probe

changes in the free volume of a polymer membrane (Jansen et al. 2009). Different aging mechanisms have been proposed. Harms claims that free volume elements diffuse towards the surface of the polymer (Harms et al. 2012). However, due to the very low expected diffusion coefficient of this process, it is significant only in the case of thin layers. McCaig et al. proposed that the aging consists of two distinct processes (McCaig and Paul 2000): (i) thickness independent lattice contraction and (ii) thickness dependent diffusion of free volume. Usually, the polymer chains pack more efficiently during physical aging and the polymer becomes denser, resulting in a decrease in permeability and an increase in selectivity. Many approaches have been used to overcome physical aging and to prepare time-stable material, such as crosslinking and addition of fillers. Lau et al. showed that addition of an ultraporous additive can prevent the effect of aging on the transport properties of super glassy polymer membranes (Lau et al. 2014).

Anomalous Transport

As already anticipated, Fick's first and second laws give a rather simplified representation of diffusion in polymers, which usually applies only to permanent gases at low pressures. In the majority of cases, the diffusion coefficient is not a constant, because of mutual interactions between the permeating species, giving rise to clustering (Jansen et al. 2011) and interaction between the polymer and the permeating species, "immobilizing" the latter (Mason et al. 2014) or plasticizing the polymer (Lo et al. 2010) and favoring diffusion. The solubility of gases and vapors in the polymer matrix is usually only constant at very low gas pressure or vapor activity. As a result, the simple expression for the solution diffusion model in Eq. 3 becomes concentration dependent:

$$P(c) = D(c) \cdot S(c) \quad (24)$$

This anomalous behavior becomes even more complex in the case of mixed gas or vapor permeation, where there may also exist a coupling effect between the different species in the mixture.

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Gas–Liquid Exchangers Using Membrane as Interface

► Gas–Liquid Membrane Contactor

Gas–Liquid Membrane Contactor

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Synonyms

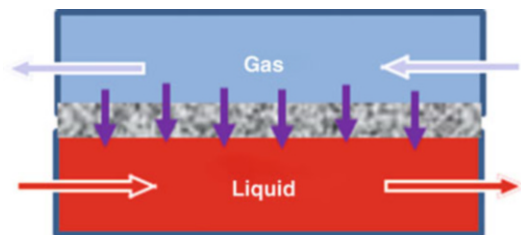
Gas–liquid exchangers using membrane as interface; Nondispersive gas–liquid contactor

History

Gas–liquid contactors are devices which are designed to promote mass transfer between a gas phase and a liquid phase, thanks to gas–liquid contact. Among the various types of existing contactors, e.g., valve trays, random or structured packing, demister, vacuum towers, etc., and membranes, one can clearly distinct two categories: firstly, contactors requiring a straight mixing between the gas and the liquid phases and, secondly, contactors where the direct physical contact between the two phases does not exist, i.e., a contactor which does not need dispersion of one phase into the other one to be efficient (Fig. 1).

Up to now, membrane contactors are the only example of the second category, i.e., systems which are simultaneously able to avoid phase mixing while promoting mass transfer. Obviously the higher the membrane permeability, the better is mass transfer efficacy. Currently, most of the industrial applications are using microporous membrane contactors (Liqui-Cell® 2014).

Like with other gas/liquid contactors, the mass transfer obtained by means of contactors can be

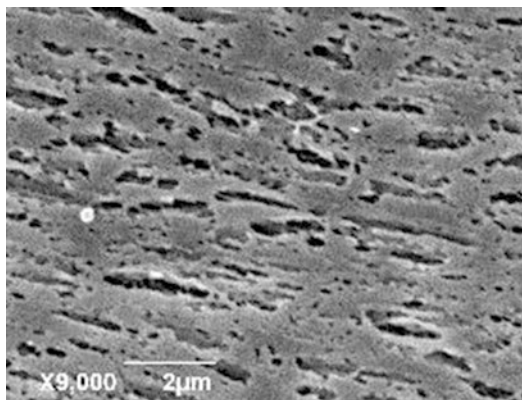


Gas–Liquid Membrane Contactor, Fig. 1 Schematic representation of a G/L membrane contactor

directed to carry out either separation and purification operations of a gas mixture by the selective removal of a given gas component or, conversely, absorption of gas (e.g., N_2 , O_2 , O_3 , etc.) in the liquid phase. The driving force is the gas partial pressure according to the Henry law: $p_i = Hx_i$ with p the partial pressure, x the concentration of gas at equilibrium, and H the Henry law coefficient. Note also that the driving force of the mass transfer can also be due to a chemical reaction between the gas species and the liquid phase.

Phenomenon

In the 1980s, Qi and Cussler (1985) achieved pioneering work devoted to the understanding of mass transfer in gas–liquid membrane contactors. Within this specific type of contactors, the membrane is primarily a physical barrier between a gas phase and a liquid phase. So to get an efficient device, a proper choice of membrane and operating conditions must be done to ensure a high level of mass transfer. For the membrane selection, it turned out that a microporous structure looked to be the best one to gather appropriate mechanical properties and high mass transfer coefficient. Most of the time, the liquid phase used is an aqueous phase; hence, it logically orientated the selection of membranes to hydrophobic rigid polymers, i.e., glassy or semicrystalline structures, like polypropylene (PP) (Fig. 2), polyvinyl difluoride (PVDF), or Teflon. Thus the aqueous phase cannot enter spontaneously the small pores ($\approx 0.1\text{--}1.10^{-6}$ m) of the membrane structure, as predicted by the Young–Laplace equation given below. Nevertheless, the main concern with a



Gas–Liquid Membrane Contactor, Fig. 2 Microporous polypropylene

microporous membrane contactor is to avoid pore wetting by the liquid phase, because pore wetting would induce a detrimental decrease of the overall mass transfer coefficient (Fig. 3a, b). In case of pore flooding, the mass transfer coefficient can drop by a factor 1,000–10,000.

Hence there is a breakthrough pressure to be respected; this limiting pressure (Δp) difference between the two phases can be calculated by the Young–Laplace equation (Kim and Harriott 1987):

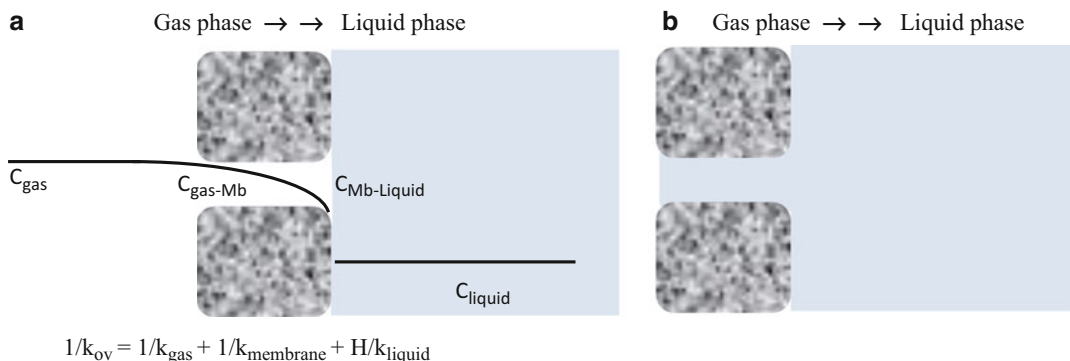
$$\Delta p = -4\gamma_L \cdot \cos \theta / d_{\max} \quad (1)$$

with γ_L the surface tension of water, θ the contact angle, and $d_{\max}$ the diameter of the biggest micropores.

As a guide, using pure water ($\gamma_L = 72.8$ mN/m at 20 °C) and PP (with pore $d_{\max} = 1$ μm and $\theta = 115^\circ$), the breakthrough pressure is 1.23 bar. However in reality, the measured breakthrough pressure is often much lower due to the presence of impurities or organic solutes in the water; any alteration of the polymer surface properties can also lower this value. On the other hand, to avoid any gas bubbling in the liquid phase, a slight overpressure is usually applied at the membrane liquid interface.

Mass Transfer Theory

As one can expect, the mass transfer extent is closely related to the operating parameters, i.e.,



Gas-Liquid Membrane Contactor, Fig. 3 (a) In a nonwetted porous membrane, the membrane transport occurs in gas-filled pore. (b) In a wetted porous membrane, the membrane transport in liquid-filled pore is much slower

mainly gas partial pressure in each phase, temperature, gas and liquid flow rates, hydrodynamic conditions, and the specific transfer area. To achieve a given purification target, the mechanism of the gas/liquid transfer must be known and used to model the mass transfer and thus to predict adequate operating parameters.

The performance of the mass transfer can be related to the variation of gas composition either between the inlet and the outlet of the gas phase or between the inlet-dissolved gas and the outlet-dissolved gas of the liquid phase. For a fast reaction with a steady gas phase velocity, the same basic equations, which are used to predict transferring gas in conventional columns, also apply for membrane contactors as recalled below:

$$\frac{C_{Gout}}{C_{Gin}} = e^{-k \cdot a \cdot L / u_g} \quad (2)$$

where C_{Gout} and C_{Gin} are respectively the outlet and inlet gas concentrations, k is the overall mass transfer coefficient, L is length of the contactor, a is the contact area between the two phases, and u_g is the gas phase velocity.

Noting one can define the gas transfer efficiency $\eta = (C_{Gin} - C_{Gout}) / C_{Gin}$, thus one can write:

$$\frac{C_{Gout}}{C_{Gin}} = 1 - \eta = e^{-k \cdot a \cdot L / u_g} \quad (3)$$

It is worth noting that modeling the mass transfer properties of a membrane contactor is even easier than with conventional contactors because the

gas/liquid contact area is well known and remains constant whatever the gas or liquid flow rates.

As shown in Fig. 3, the overall mass transfer resistance is due to the successive resistances of the gas phase, of the membrane, and of the liquid phase. Clearly the analogy can be made with electrical resistances, and the reciprocal of the overall mass transfer coefficient (k_{ov}) can be written as the sum of the individual mass transfer coefficients:

$$1/k_{ov} = 1/k_{gas} + 1/k_{membrane} + H/k_{liquid} \quad (4)$$

H being the Henry law constant between the gas and liquid phases.

Pros and Cons

Compared to conventional gas/liquid contactors (tower, packed columns, mixer settler), membrane contactors are known to avoid a number of drawbacks due to phase dispersion such as solvent loss, foaming, unknown specified area, and column flooding. It is worth also to underline that as polymer is the core of membrane contactors, one can get a strong reduction in weight of the equipment compared to conventional ones. At last one can note as well that a membrane contactor can be installed horizontally or vertically without problems and that its efficiency is not dependent of roll and pitch marine.

Note that liquid-liquid extraction can also be achieved using membrane contactors, hence avoiding any hazard of emulsion formation.

All these advantages are linked to the mixing nondispersive feature of a membrane contactor.

On the other side, drawbacks can come from the facts that the pores of a membrane do not have the same size, that pore fouling can occur and block the transfer, and that the hydrophobic properties of the surface can be altered inducing a dramatic decrease of the breakthrough pressure.

Intensification Potential of Mass Transfer

As with any membrane modules, the membrane contactors can be prepared with different geometries, going from plate and frame modules, spiral modules, or hollow fiber modules. The last type has received the most attention because it allows the creation of very large interfacial areas, up to $10,000 \text{ m}^2/\text{m}^3$ that is up to 20-fold the interfacial area of a structured packed column (Gabelman and Hwang 1999; http://docnum.univ-lorraine.fr/public/INPL/2011_NGUYEN_P_T.pdf6). Thus the factor **k.a.**, which is one of the key parameters predicting the mass transfer efficiency (Eq. 3), indicates clearly that for a constant value of **k**, a strong intensification of the transfer can be reached with membrane contactors.

This high value of area will be obtained with fibers having very low inner diameter, typically in the 50–100 μm range. Hence, a limit of the transfer with membrane contactor can now be foreseen: the increase of the specific area shall correspond to an increase of the pressure drop in the fibers of smaller diameter. This drawback will be amplified by using fluid of high viscosity.

Thus the potential of intensification is also strongly linked to the hydrodynamic conditions prevailing in the contactor. This shall depend merely on the nature of the fluid circulating in the lumen of the fibers.

Applications

As example of separations, acid impurities of flue gases like SO_x, NO_x, or even CO₂ can be

removed by contacting the gas feed flow with a liquid properly chosen to trap the acidic species. The gas removal can be due to a physical chemical dissolution of the acid gas into the liquid or to a chemical reaction with the liquid; in this case, the liquid must be endowed of basic properties or contains a solute which is itself a base. When the principle of gas removal is linked to physical chemical affinities, it is wise to operate under pressure to promote higher solubility of the gas into the liquid. On the other case, if a chemical reaction is involved between the gas and the liquid, pressure is not a key parameter.

As example of gas dissolution, one can cite nitrogenation in the beverage industry or blood oxygenation. It is worth to note that blood oxygenation has been one of the very first examples of using membrane contactors in 1975 (Esato and Eiseman 1975); currently the total annual market is above €500 million.

Some examples of use of membrane contactors are listed here:

- Liquid degassing: O₂, CO₂, and N₂ removal from liquids, used for carbonation (food and beverage industry), nitrogenation (microelectronics), deoxygenation, etc.
- Bubble-free gas/liquid mass transfer primarily for ozonation of semiconductor cleaning water
- Dehydration
- Blood oxygenator (health sector)

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Genotoxin Removal

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Synonyms

Degenotoxification

Definition

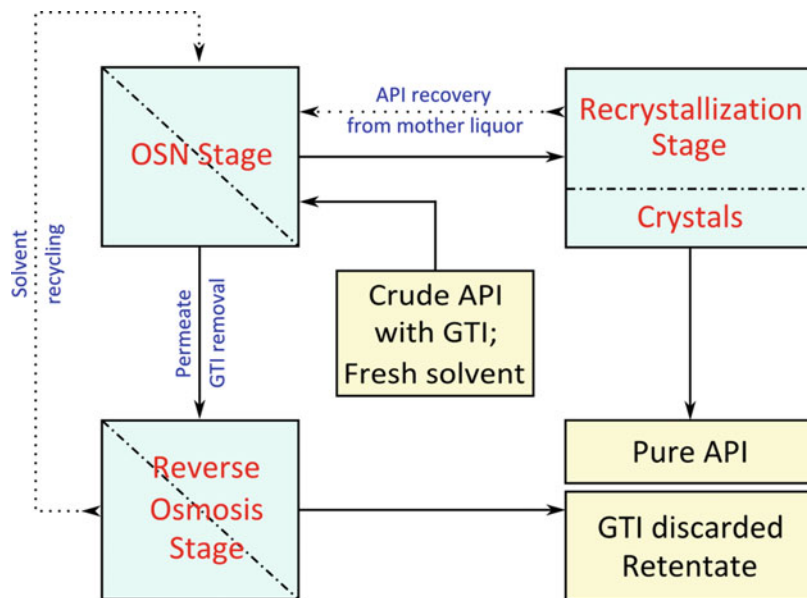
Genotoxin removal by membranes is an emerging purification technology aiming to reach ultralow genotoxic impurity levels in order to address health and environmental regulations.

Characteristics

The main challenge of genotoxin removal by membranes lies in the fact that most of them are highly reactive species and thus can attack polymeric membrane framework at molecular level. Degenotoxification of active pharmaceutical ingredients (API) is of utmost importance to drug manufacturers. Genotoxicity of pharmaceutical impurities is being continuously evaluated increasing the list of such highly toxic impurities. Pharmaceutical regulatory authorities draw the attention to API purification and strict the threshold limits of genotoxins via annually issued guidelines. Besides the conventional API downstream processes such as recrystallization, fractional distillation, chromatography, extraction, and adsorbents, new technologies are being implemented in the pharmaceutical industry. Application of nanofiltration alone and combined with adsorbents are proposed as alternative purification technologies assuring ultralow genotoxin contaminations in drug products. API post-reaction streams usually feature organic solvents, limiting the selection of membranes to be used in the process. Commercially available

polymeric and ceramic membranes stable in organic solvents include Koch SelRO, Evonik DuraMem series, SolSep NF series, Borsig GMT-oNF series, as well as Inopor and Pervap ceramic membranes. The feasibility of API degenotoxification by organic solvent nanofiltration (OSN) has been successfully applied in diafiltration mode where fresh solvent is continuously added to the retentate in order to push the relatively small genotoxic molecules through the membrane, while the relatively large API molecules are retained as depicted in Fig. 1 (Szekely 2011). The aim is achieving high genotoxin removal and low API loss which mainly depends on the molecular size gap between the impurity and the API as well as the polarity of the impurity. Hybrid processes featuring OSN and adsorbents have been developed for the removal of genotoxic palladium, impurity retained (Pink 2008), and 1,3-diisopropylurea, API retained (Szekely 2012), from post-reaction solutions. In the former case, the Suzuki post-reaction solution was subjected to OSN, and the palladium was retained by the membrane, while the API was collected in the permeate. On the contrary, in the latter case, the genotoxin was removed with the permeate, while the API was retained. In both cases the genotoxin levels were reduced further by using commercially available adsorbents or tailor-made molecularly imprinted polymers. Not only has the combination of molecular imprinting and membrane technology provided an efficient genotoxin removal process but their fusion as well. Molecularly imprinted membranes (MIM) can also be used for API degenotoxification. Potentially genotoxic 4,4'-methylenedianiline has been applied as a template for MIM adsorbents (De Luca 2011). Environmental and economic analysis proved the sustainability of API degenotoxification by membrane processes in comparison with conventional API purification methodologies such as chromatography and recrystallization (Szekely 2013). Besides pharmaceutical purification, control of genotoxins is also an environmental concern. Nanofiltration featuring DESAL 51 HL, DESAL 5 DL, UTC-20, and UTC-60 membranes was applied for the removal of genotoxic

Genotoxin Removal,
Fig. 1 Scheme of
 genotoxin removal by OSN
 with potential reverse
 osmosis for solvent
 recycling



atrazine – banned as a total herbicide in Europe since 1991 – from different water matrices including distilled water, tap water, and river water (Zhang 2004).

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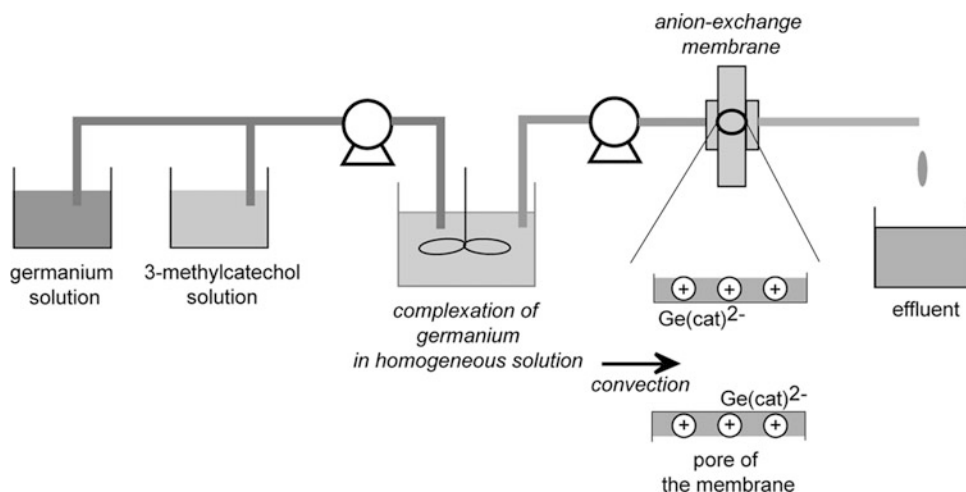
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Germanium Recovery by Ion Exchange Membranes

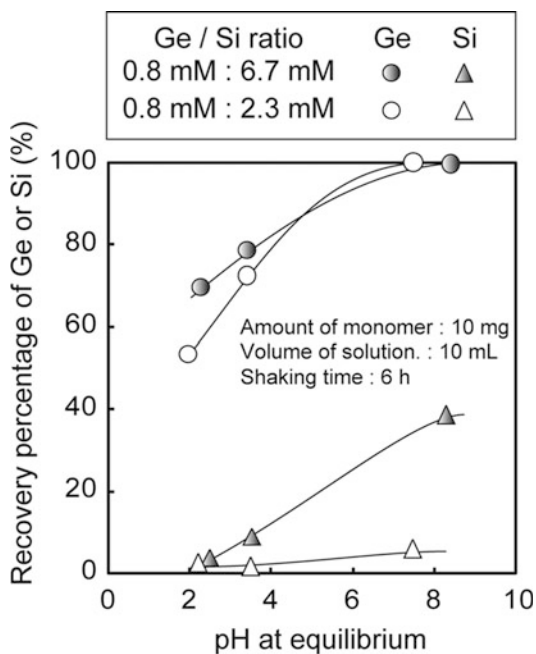
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Germanium recovery using catechol complexation and membrane permeation (also called germanium-recovery-membrane system) is the unique way to recovery germanium. Now, germanium is a rare semimetal and used for semiconductor, catalysis, and optical apparatus. Due to heightened interest in renewable energy sources, the production of solar panels has increased. In production of solar panel, germanium is doped to silicon compound to change the energy gap. Processing of solar panel production generates



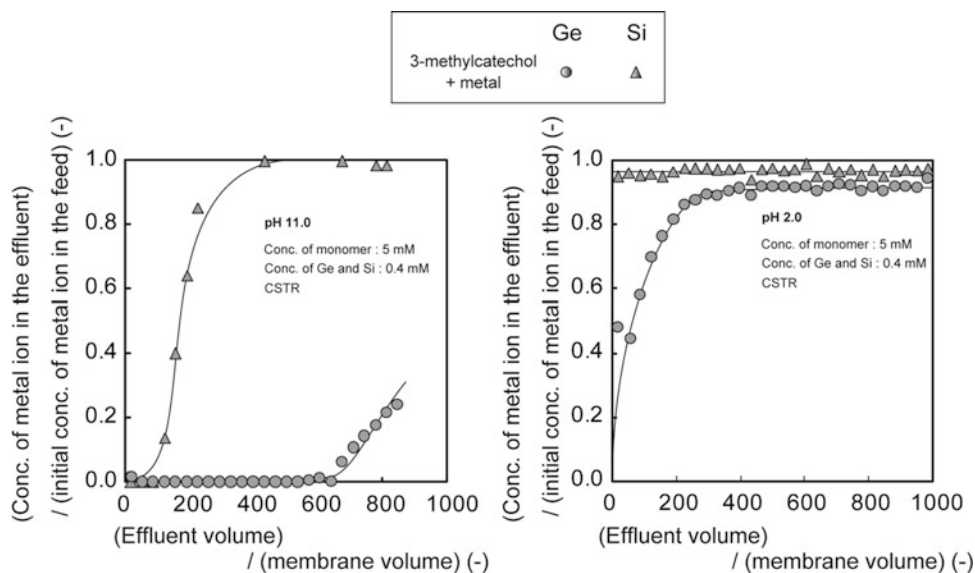
Germanium Recovery by Ion Exchange Membranes, Fig. 1 Germanium recovery system using catechol complexation and membrane permeation

the mixed waste of germanium and silicon. For recycling, germanium as a rare metal should be recovered from germanium-containing waste. Using the polymerization technique, the functional group, polyol group, was introduced to the polymerized resin to recovery germanium along with the diffusion. The polyol-containing polymer brush was introduced to the membrane and the germanium solution was flown through the membrane, achieving the high-speed recovery via convection. Catechol forms the complex with germanium as an anion. This complexation occurs selectively compared with silicate ion. We propose the germanium recovery system using membrane and resin, as shown in Fig. 1 (Nozoe et al. 2012): (1) germanium ion selectively forms the complex with catechol in solution, forming anion complex, and (2) germanium complex was captured to the quaternary-amino-group-introduced porous membrane and resin. This study addresses the selective complexation of germanium in the solution and the recovery of anion complex with membrane and resin continuously. In the presence of silicate ion, pH dependence of germanium recovery was checked in a batch mode, as shown in Fig. 2. In lower pH, the selective recovery against silicate ion was achieved in changing the concentration ratio, because the complex formation easily forms in lower pH region. In continuous mode, we determined the breakthrough



Germanium Recovery by Ion Exchange Membranes, Fig. 2 pH dependence of germanium recovery against silicate ion in a batch mode

curves at the initial pH of 2.0 and 11.0, as shown in Fig. 3. At pH 11.0, germanium ion was adsorbed more compared with that at pH 2.0, while the selectivity against silicate ion was higher. This process is applicable for the wastewater of the solar panel containing germanium.



Germanium Recovery by Ion Exchange Membranes, Fig. 3 Breakthrough curves of germanium recovery at pH of 11.0 and 2.0

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Glass Transition Temperature (T_g)

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General Introduction

At the macroscopic scale, the glass transition temperature, T_g , represents the temperature above which a material changes from a stiff glass into a viscous fluid or a rubbery material. Besides polymers, which are the most common materials with a glass transition temperature, also various amorphous solids, organic liquids, alloys, or inorganic glasses may exhibit a glass transition.

At the molecular scale, the T_g of a polymer is the temperature above which large segmental motions of the polymer chains become possible within the time scale of the experiment. The glass transition temperature depends on the molecular architecture. Substituents that restrict the backbone rotation of a very simple polymer, such as polyethylene, will increase its T_g , and the presence of polar groups will have an even stronger effect (Table 1). Besides the substituents on a flexible polymer backbone, the chemical structure of the backbone itself obviously has a major impact on the glass transition temperature. The presence of sterically hindered groups, conjugated bonds, fused rings, etc., increases the glass transition temperature significantly. In the extreme case, the mobility is so much restricted that a T_g is no longer observed. For instance, polymers of intrinsic microporosity (PIMs), a novel class of polymers with growing interest for their high gas permeability (McKeown and Budd 2010), consist of ladder structures with such a high rigidity that large-scale motions are impossible and they do not exhibit a glass transition below their degradation temperature.

Glass Transition Temperature (T_g), Table 1 Glass transition temperature of polymers $[-CH_2CH(R)-]_n$ with the same backbone and different substituents R (Brandrup et al. 1999)

Polymer	R	T_g
Polyethylene	H	155
Polypropylene	CH ₃	258–270
Poly(vinyl fluoride)	F	314
Poly(vinyl chloride)	Cl	354
Poly(vinyl alcohol)	OH	358
Polystyrene	C ₆ H ₅	373
Poly(vinyl acetate)	CH ₃ COO	305

The glass transition temperature of polymer blends depends on their miscibility. In the rare case of miscibility at the molecular level, the glass transition of the blend has a value between those of the neat polymers. Different equations describe the behavior of polymer blends more or less satisfactorily.

In the Fox equation, the T_g of the blend depends exclusively on its composition:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

where w_1 and w_2 are the weight fractions and $T_{g,1}$ and $T_{g,2}$ are the glass transition temperatures of pure polymer 1 and polymer 2, respectively.

The Gordon-Taylor equation is able to describe slightly asymmetric dependencies of the T_g on the blend composition, by means of an adjustable parameter, K_{GT} :

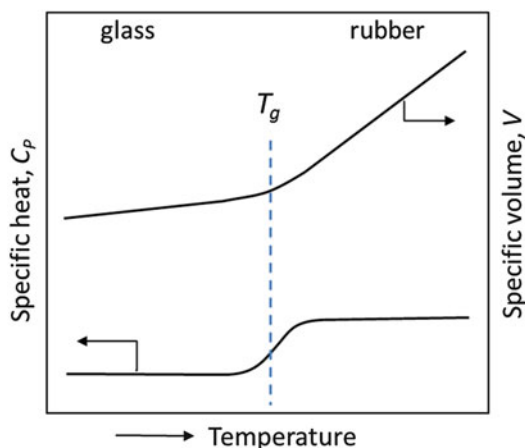
$$T_g = \frac{w_1 T_{g,1} + K_{GT} w_2 T_{g,2}}{w_1 + K_{GT} w_2} \quad (2)$$

The Kwei equation introduces a binary parameter, q , which represents the interaction between the two polymers, and can be used to describe even more asymmetric T_g versus composition profiles (ElMiloudi et al. 2009):

$$T_g = \frac{w_1 T_{g,1} + K_{Kwei} w_2 T_{g,2}}{w_1 + K_{Kwei} w_2} + q w_1 w_2 \quad (3)$$

Glass Transition Temperature Analysis

Besides a change in the mechanical properties, the T_g is also accompanied by a fairly abrupt change



Glass Transition Temperature (T_g), Fig. 1 Schematic representation of a DSC trace (bottom) and of the specific volume (top) of an amorphous polymer

in the specific heat of the sample (Fig. 1). Various other properties undergo more or less pronounced changes at the T_g , such as the density, the specific heat, the elasticity coefficient or Young's modulus, the rate of diffusion of gases or liquids through the polymer, the thermal expansion coefficient, etc.

There is a clear correlation between the glass transition temperature and the transport properties in dense membranes (Matteucci et al. 2006). The gas and vapor permeability is much higher in the rubbery state than in the glassy state, and the selectivity is usually lower. Therefore, the value of the T_g is one of the main parameters influencing the membrane performance. For most other membrane applications, also those using porous membranes, the glass transition temperature is of large interest too. Since porous membranes may collapse upon softening, it is of fundamental importance that they are operated at a temperature sufficiently far below the T_g .

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Glass Transition Temperature Depression

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Glass transition temperature depression is the phenomenon which describes the reduction of the glass transition temperature by external factors, usually by the presence of solvent molecules or of other additives in the polymer matrix. Such additives have the capacity to enhance the mobility of the polymer chains, thus enabling long range motions at lower temperature than in the neat polymer. Although this often goes hand in hand with the phenomenon of plasticization, a reduction of the elastic modulus at room temperature, the two concepts should not be confused. Plasticization strictly refers to the mechanical properties of the polymer and the molecules, which reduce the elastic modulus of a polymer by an increase of the chain mobility generally also reduce their glass transition temperature. The opposite is not necessarily the case and it may happen that an additive, which lowers the T_g , at low concentration increases the elastic or Young's modulus at room temperature. This is then referred to as anti-plasticization.

Glassy Membranes

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Glassy membranes are membranes consisting of amorphous polymers which are in their glassy state at room temperature or under the normal operation conditions, i.e., their glass transition temperature is above room temperature or the operating temperature. The high stiffness of the glassy polymer provides sufficient mechanical strength to the membranes to exist also as porous or dense integrally skinned flat films or hollow fibers.

The polymer stiffness is an essential aspect in the membrane formation process by non-solvent induced phase inversion, where at a certain point of the process solidification of the polymer is required to consolidate the morphology of the membrane. In glassy polymers, this is typically by vitrification of the polymer when diffusion of the solvent from the polymer rich phase into the coagulation bath leads to a gradual increase of the glass transition temperature until this exceeds the coagulation bath temperature.

Glassy Polymer

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Strictly, any amorphous polymer is glassy at temperatures below its T_g , but in practice a glassy polymer refers to those polymers which are in their glassy state at room temperature, thus to amorphous polymers with a glass transition temperature above room temperature, in contrast to rubbery polymers, which have a T_g below room

temperature, and (semi-)crystalline polymers with a melting point above room temperature. Under particular circumstances also semi-crystalline polymers can become glassy after quenching, if the crystallization kinetics and the crystal nucleation rate are sufficiently slow to prevent crystallization upon rapid cooling. A typical example of such polymer is poly(ethylene terephthalate), PET.

Glassy polymers are characterized by their high stiffness and amorphous non-crystalline structure. These properties make them size selective in their dense form and also mechanically sufficiently resistant to exist as porous flat film or hollow fibre membranes. Examples of the most commonly used polymers in commercial membranes are cellulose acetate, polysulfone, poly(ether sulfone), polyimide, and polycarbonate.

Global Optimization of Membrane Processes

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For a number of years, researchers and engineers in many fields have reported the problem of obtaining multiple solutions while solving problems of nonlinear programming (NLP). Multiplicity of solutions is caused by the nonconvex nature being present typically in many engineering problems. Global optimization (GO), sometimes called nonconvex optimization, encompasses several techniques which can be used to handle the problem of finding the best of these solutions, the global optimum.

General form of GO problem is same as for NLP problem and it may be stated as

$$\begin{aligned} \min_x & f(\mathbf{x}) \\ \text{s.t.} & \mathbf{h}(\mathbf{x}) = 0 \\ & \mathbf{g}(\mathbf{x}) \leq 0 \end{aligned}$$

where $\mathbf{x}$ represents vector of optimization (decision) variables, $f(\mathbf{x})$ is optimization criterion, $\mathbf{h}(\mathbf{x})$ and $\mathbf{g}(\mathbf{x})$ stand for vectors of equality and inequality constraints, respectively.

To find the global optimum, many methods have been developed. These can be basically classified into two branches, stochastic and deterministic ones. Stochastic methods (Weise 2007) such as simulated annealing, genetic algorithms, and particle swarm optimization got inspired by natural phenomena. In general, they randomly search through the solution space (space where constraints are satisfied) and due to that usually do not require gradient information. It is often reported that weakness of these algorithms is that they cannot guarantee convergence to global optimum in finite time.

On the other hand, deterministic methods search through the whole solution space systematically and thus can provide so-called ϵ -convergence (ϵ is arbitrarily small positive number) guarantee to the global optimum. Most popular are methods based on branch-and-bound algorithms and interval analysis (Horst and Tuy 1990).

The latter type of methods was successfully used in Chen et al. (2006) for globally optimal design of membrane fuel cell. Other applications of methods of GO involve parameter estimation (Papamichail and Adjiman 2004), optimal control problems (Esposito and Floudas 2000), and problems of nonlinear and mixed integer nonlinear programming (Chachuat et al. 2006). Other references on GO problems in chemical engineering can be found in Rangaiah (2010).

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Gluconic Acid Production in Hybrid System Membrane Bioreactor with ED

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Synonyms

Organic acid production by membrane biotechnology with electrodialysis (ED)

Introduction

Organic acids are a group of organic compounds with acidic properties. The most common organic acids are the carboxylic acids (e.g., gluconic acids) containing carboxyl group -COOH and sulfonic acids comprising the group $\text{-SO}_2\text{OH}$. In addition, organic compounds, which have hydroxyl -OH , thiol group -SH , the enol group, and the phenol group that present weak acidity, are also generally referred to as organic acids. Organic acids have been widely used in foods, beverages, pharmaceuticals, cosmetics, detergents, plastics, resins, and other biochemical or chemical products. As a result, they have a close relationship with human's daily life. As one type of organic acid, gluconic acid has been used as food additive, acidity regulator, and chelating agent. Organic acids can be produced by two prevailing

methods, i.e., fermentation and chemical synthesis. In either fermentation or chemical synthesis, separation, concentration, and purification are necessary for the acid production. Due to the excellent performance of membrane separation, membrane technology such as electrodialysis (ED) can provide a novel alternative to conventional procedures for organic acid production (Huang et al. 2007).

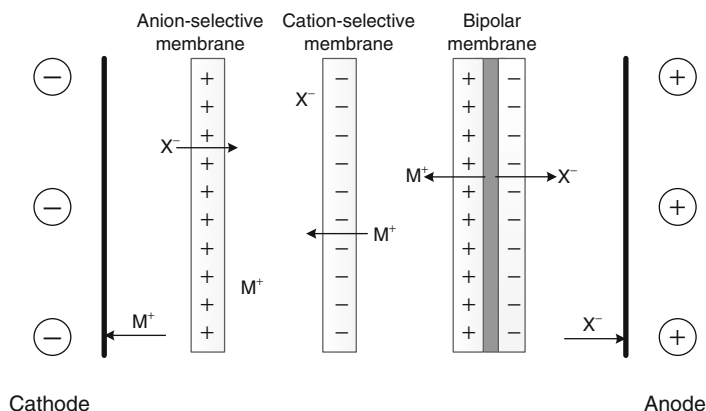
ED is a kind of technology which arranges ion-exchange membranes alternately in a direct current field (see Fig. 1). The ion-exchange membranes include cation-selective, anion-selective, and bipolar membranes. ED technology includes conventional electrodialysis (CED), electrometathesis (EMT), electro-ion substitution (EIS), electro-electrodialysis (EED), electrodialysis with bipolar membranes (EDBM), electrodeionization (EDI), and two-phase electrodialysis (TPED), which can be applied for organic acid production (Huang et al. 2007).

Electrodialysis with bipolar membranes (EDBM) has been proved to provide a feasible solution for gluconic acid production (Novalic et al. 2000). EDBM is a kind of technology that integrates solvent and salt dissociation. Compared to conventional organic acid production (precipitation and acidification), it can realize salt conversion without second salt pollution or provide H^+ and $\text{OH}^-/\text{alkoxide}$ ions in situ without salt introduction (Huang and Xu 2006). In lab scale EDBM system for gluconic acid production, the conversion rate of sodium gluconate could reach no less than 98 %, with current efficiency around 70 % and energy consumption about 1 kWh/kg acid (Yu et al. 2000; Huang et al. 2008).

When a reactor or bioreactor is integrated with ED, the combined process can realize in situ separation, purification, and organic acid production adjustment without apparent retrogression in its function. For instance, the use of fermentation to produce acids can be integrated into a membrane bioreactor system coupled with ED. However, some improvements are needed for modifying the technology, which include reducing membrane cost (especially bipolar membrane), improving the antifouling properties of

Gluconic Acid Production in Hybrid System Membrane Bioreactor with ED,

Fig. 1 Schematic of
ED. M^+ : cation; X^- : anion



membranes, and increasing the selectivity for co-ions and developing ion-exchange membranes with a specific selectivity for organic anions or hydrogen ions (Huang et al. 2007). To sum up, membrane biotechnology with ED is a promising solution for organic acid (e.g., gluconic acid) production (See also organic acid production by membrane technology with ED).

Cross-References

- [Membrane bioreactors for treatment of tannery effluents](#)
- [Membrane biotechnology](#)
- [Ultrafiltration membrane bioreactor](#)

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Glucosidase in Membrane Bioreactor

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β -Glucosidase is the enzyme responsible for the oleuropein hydrolysis; it belongs to the group of hydrolases widely existing in various sources, such as fungi, bacteria, plant, and animal tissue. The broad optimum pH and temperature range makes this enzyme particularly useful for application in biotechnology processes. The β -glucosidase from different sources has been studied in various systems, as free or attached to different supports (Yeoh 1991; Esen 1993; Montero and Romeu 1993).

A lot of interest was demonstrated in the enzymatic/substrate system β -glucosidase/oleuropein due to the fact that the oleuropein hydrolysis products are phytochemicals that can be potentially used, if obtained in pure form, in pharmaceutical and food field. In addition oleuropein hydrolysis is very important because it is present in Olive Mill Waste (OMW), following the strategy of waste valorization.

In *in vivo* system, olives and leaves, oleuropein is hydrolyzed by β -glucosidases action. In the first reaction step, the products are oleuropein aglycon with a glucose molecule. Oleuropein aglycon, due

to its poor water solubility, is not yet purified and not yet commercially available, because after its production by enzymatic hydrolysis, it is fastly rearranged into water-soluble compound.

Few examples are reported in the literature in which β -glucosidases are used immobilized on membranes (Mazzei et al. 2009).

A hybrid membrane operation system is developed to (i) compartmentalize the oleuropein hydrolysis, occurring in aqueous phase within the porous membrane, and (ii) separate and stabilize the aglycon, occurring in organic phase at the membrane lumen side interface, based on the membrane emulsification concept.

The biotechnology used to conduct the hydrolysis of oleuropein is a multiphase biocatalytic membrane reactor.

Polymeric membranes were heterogenized with a β -glucosidase. The OMW, containing oleuropein, passed through the enzyme-loaded membrane where the reaction occurred. The water phase containing reaction products passed through the membrane and met an organic phase recirculated into the lumen side where water-in-oil emulsions were formed drop by drop. Droplet size and stability were adapted so that enough exchange area interface was achieved, and once aglycon extraction was completed, droplets broke and phases separated spontaneously. The integrated system biocatalytic membrane reactors and membrane emulsification process showed that it is possible to produce and simultaneously isolate the isomer of oleuropein aglycon in one step, starting from OMW (Mazzei et al. 2009, 2010, 2012; Conidi et al. 2014).

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Gold Recovery by Supported Liquid Membranes

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Gold is the chemical element which symbol is Au (from Latin *aurum*) and the atomic number is 79. The oxidation states in its compounds range from -1 to $+5$, and Au(III) is the most common. Typical Au(I) complex is $\text{Au}(\text{CN})_2^-$ (in cyanide media) which is the soluble form of gold encountered in mining, while in chloride media Au(III) complexes (Au_2Cl_6) are the typical ones.

Gold production by means of its extraction from mining can represent an important contribution to environmental pollution. Metal ores, which generally contain less than 1 ppm of gold, are ground and mixed with sodium or potassium cyanide for gold chemical extraction. Precious metal and heavy metal impurities such as cadmium, lead, zinc, copper, nickel, and arsenic are usually present in an anionic form (i.e., cyanide salts) after their extraction from metal ores. These salts are toxic to the liver and kidneys because of both cyanide and metal content.

Thus, it would be desirable to be able to selectively remove these complexes for the recovery of precious metals.

Gold, over its use in jewelry, also has a wide use in various industries, thanks to its physical and chemical properties. Thus, the recovery of this metal from the different wastewater generated by these industries is also of growing interest (Alguacil 2004).

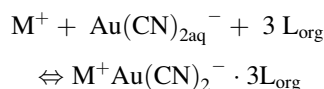
Gold can be recovered from different aqueous solutions by various physicochemical separation techniques as precipitation, ion exchange, carbon adsorption, cementation, solvent extraction, etc. In the case of convective solvent extraction, metal ion-containing solution is placed in contact with a large amount of an appropriate organic phase (Kargari et al. 2004). This extraction step is followed by a stripping one. The main drawback of solvent extraction is the large amount of solvent required when dilute solutions were processed, making this process not very cheap and safe, since the used solvents are often chlorinated and sometimes carcinogenic.

Liquid membrane (LM)-based processes have become an attractive alternative to conventional techniques for selective separation and concentration of both organic and inorganic compounds from dilute aqueous solutions since they combine extraction and stripping into a single process, thus reducing the solvent inventory requirement and then cost significantly (Molinari and Argurio 2011). They also allow the use of expensive and highly selective extractants, which otherwise would be uneconomic in solvent extractions.

LM systems include nonsupported liquid membranes (bulk liquid membrane (BLM) and emulsion liquid membrane (ELM)) and supported liquid membrane (SLM). SLMs consist of an organic LM phase impregnated in a thin hydrophobic microfiltration membrane. This LM phase generally contains an extractant (carrier) which binds very selectively the target component in the donor phase (feed), transporting it into the acceptor phase (strip), resulting in the so-called facilitated transport (Molinari et al. 2009a, b).

Referring to gold transport, SLM systems have been tested in the separation of this precious metal mainly from cyanide (Au(I)) or chloride (Au(III)) media. Highly acidic conditions are required for the extraction and transport of Au(III) because of its easily reducible nature.

Various carriers for Au transport across a SLM were reported in literature. Among them, the commercially available extractant Cyanex[®] 921 has been applied in the carrier-facilitated transport of both gold(I) and gold(III) recovery from cyanide and chloride media, respectively (Alguacil et al. 2005). Gold(I) is transported from alkaline pH values (6–11). Gold(I) extraction takes place in that pH range by the following equilibrium reaction:



where the subscripts aq and org denote the species contained in the aqueous and organic phase, respectively, and L represents the extractant.

In the case of gold(III), the extraction is governed by the following pH-dependent equilibrium reaction:



where $n = 1, 2$.

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Graft Polymerization

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Graft polymerization is a process in which monomers are covalently bonded and polymerized as side chains onto the main polymer chain (the backbone).

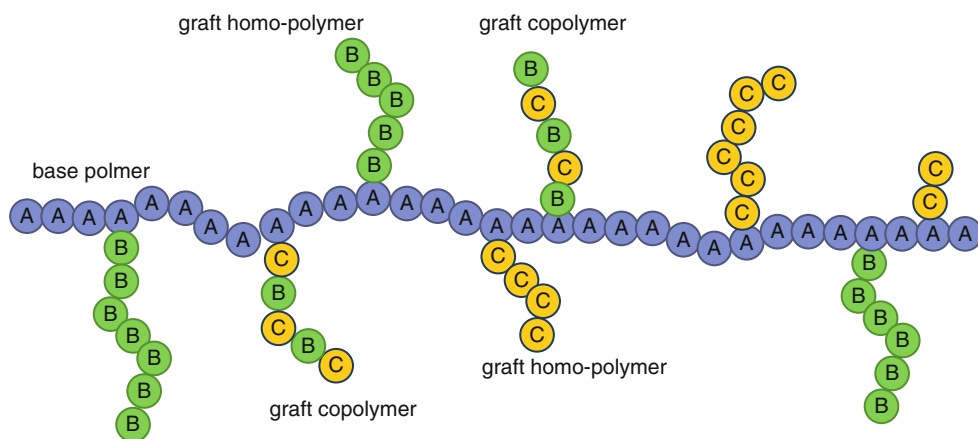
Grafting is an attractive approach to impart a variety of functional groups to a polymer. Graft polymers are also known as graft copolymer since it contains at least two different kinds of monomer units such as the grafted side chains that are structurally distinct from the main chain. The monomer to be grafted may be of one or more than one type; thus, the graft chains in grafted copolymer may be

homo-polymers or copolymers as illustrated in Fig. 1 (A, B, and C are representing different types of monomers).

Grafting can be accomplished by either “grafting to” or “grafting from” approaches. In “grafting to” approaches, functionalized monomers react with the backbone polymer to form the grafted one. On the other hand, “grafting from” is achieved by treating a substrate with some method to generate immobilized initiators followed by polymerization. High grafting density polymer also can be accomplished using this technique (Bhattacharya et al. 2009).

Graft copolymerization can be initiated by various methods including chemical treatment, photochemical treatment, ionizing radiation (such as gamma radiation, electron beam radiation, etc.), photo-irradiation, plasma-induced techniques and enzymatic grafting, etc. Grafted polymers can be very useful as they can be tailored to the requirements of particular applications by appropriate selection of backbone and monomers to be grafted.

Grafted polymers have wide range of application such as in the field of biomedical, textiles, automobiles, cable technology, separation and purification, electrolyte membranes, coatings, adhesives, laminates, commodity plastics, etc.



Graft Polymerization, Fig. 1 Structural representation of graft copolymer

Cross-References

► Surface Modification: Chemical Treatment

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Grain Models

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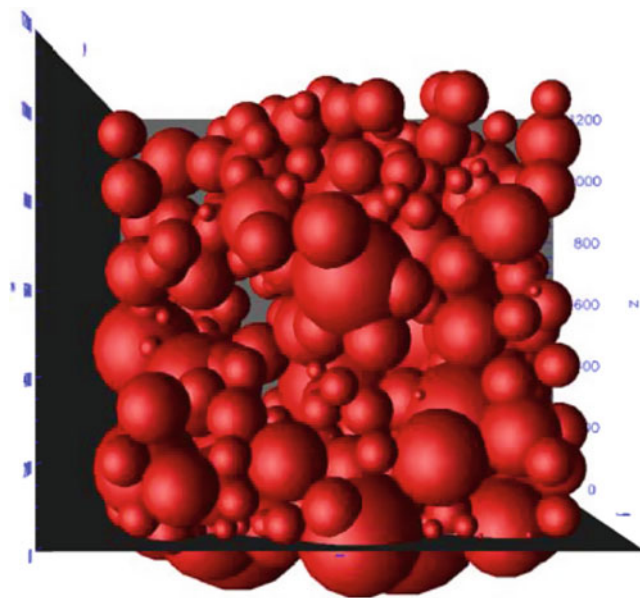
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Grain models involve a set of grain-shaped objects to represent the solid phase in the interior of porous materials. Model representation of the structure of porous membranes is very important for visualizing and understanding the structure of amorphous, porous, and random membrane materials and can be implemented, among other ways, by deterministic or stochastic modeling of the outcome of the actual fabrication process (e.g., random assembly or sequential deposition of particles) with or without reference to the detailed physics of the process (Preparata and Shamos 1985). Typically, such reconstructions involve some random packing, optionally combined with ballistic deposition of hard or soft spheres, disks, or ellipsoids of prolate or oblate geometry (Rogers 1964). This stage is usually followed by simulation of grain sintering as the result of thermal or viscous sintering. In the majority of packing procedures, random sequential deposition of overlapping or non-overlapping particles takes place (Jaeger and Nagel 1992). The particles position themselves either randomly or under the influence of some unidirectional force (ballistic) or,

alternatively, toward some fixed center of attraction (Finney 1970). Ballistic random sphere packs are usually driven by gravity and are considered to be more representative of the compaction process. Ballistic deposition and central attraction methods provide packings with similar structural properties in terms of the autocorrelation function. Depending on the type of fabrication process as well as on the characteristic dimensions of the grains, other forces, either local/short ranged (van der Waals, double layer, hydrodynamic) or long ranged (electrostatic, electromagnetic), can also be taken into account during simulations. One, two, or three points of contact can be assumed to discontinue the downhill motion of the particle. In energy-based models, downhill motion of a particle continues until a position of local energy minimum is reached that is considered stable. Such a procedure can be systematically followed through the use of a steepest descent method followed by a conjugate gradient algorithm (Conway and Sloane 1993). Procedures based on Monte Carlo or similar statistical methods have also been implemented, where each time a number of test grains are inserted, but only selected displacements are allowed that lead to minima of position or energy. Motion and interaction of granular particles have also been studied mechanistically with computational methods, such as the discrete element method (DEM), also called a distinct element method (Zhu et al. 2007, 2008), for computing the motion and effect of a large number of small particles. Although DEM is closely related to molecular dynamics, the method is generally differentiated by its inclusion of rotational degrees of freedom, as well as compacted and other complex granular geometries. Grain models have also been used for the description of micro- or nanoparticle additives, also called nanofillers (at least one of the particles' dimensions is in the nanometer range), into a polymer membrane to form a polymeric composite membrane or a hybrid, mixed matrix membrane (Sanchez et al. 2005). This is a promising idea to improve the separation properties of the neat polymer and produce the so-called nanobarriers with numerous applications in gas separation, fuel cells, preservation of sensitive products, etc. The enhancement of

Grain Models,

Fig. 1 Ballistic reconstruction followed by partial sintering



barrier properties through the addition of inorganic nanoparticles in polymer matrices can be studied with the help of grain models and elucidate their complex dependence on interfacial interactions, filler shape and orientation with respect to the transport direction, filler size, distribution of inter-filler distances, and degree of agglomeration (Fig. 1).

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Granular Media Pretreatment Filtration

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Definitions

The term *granular media filtration* refers to the use of packed bed of granular media to provide a filtration stage between a raw water intake and a final advanced treatment stage.

Objectives

The objectives of pretreatment using a granular media filter are to remove a proportion of particulate constituents that would otherwise foul a downstream treatment stage such as reverse osmosis or ion exchange. If combined with the use of chemicals, or if the media acts as a biofilter, the granular media filtration stage can be used to reduce the concentration of dissolved organics as well.

Description

In a granular media filter, the feed passes through a packed bed of granules, and contaminants are progressively removed. Due to the ability of the filter to continue removing particles as the feed progresses through the bed, these filters are sometimes referred to as “depth filters,” though this generic description also covers other types of filtration device.

The simplest granular media filter is a sand filter. The original slow sand filters used a very low filtration velocity and relied on capturing particles on the surface where a biologically active layer formed (the “schmutzdecke” layer). Rapid gravity filters (RGF) using sand media were developed more than 100 years ago to increase filtration capacity and reduce the footprint required. These rapid sand filters used a much higher linear velocity and a deep bed of granules to increase dirt-holding capacity and convert the device from a surface filter to a depth filter (Richardson et al. 2002).

The granular media filter is a development of these early sand filters. Different types of media are combined in current commercial products to optimize performance. Generally, the filter operates with a downflow loading cycle in which particles are removed from the feedstream. A periodic cleaning cycle is then undertaken referred to as backwash in which the flow direction is reversed, i.e., normally in upflow. The flow rate during backwash is sufficient to cause the bed to expand in volume, though it is not fully fluidized. The efficiency of the backwash flow may be well enhanced by the introduction of air known as air scour.

Particle Removal Mechanisms

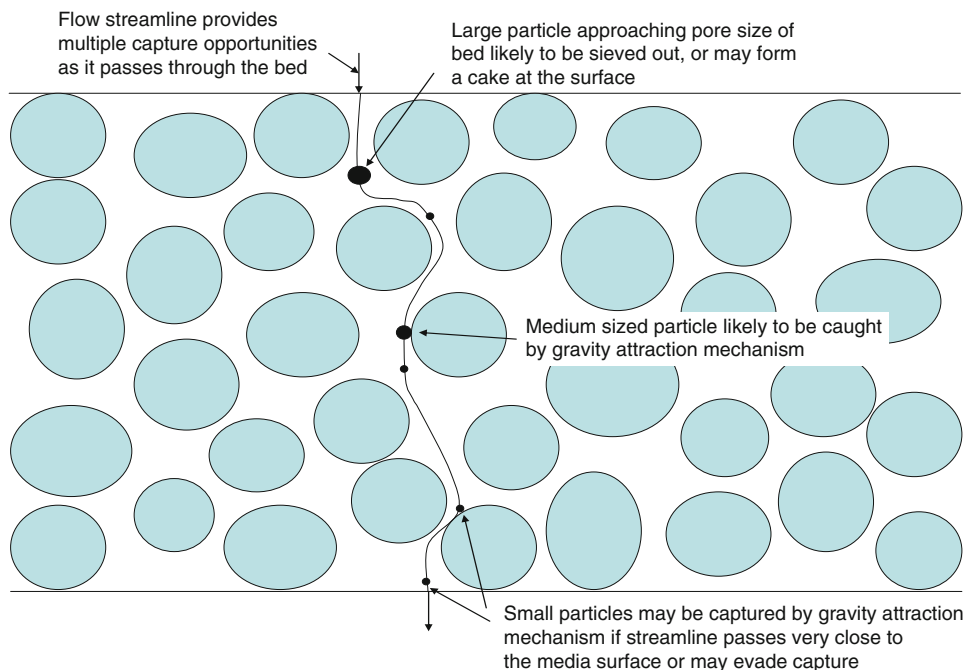
Filtration devices such as membranes or screens use a surface removal mechanism to capture particles. The smallest particle that can pass through such a filter is equivalent to the largest pore or aperture in the surface of the filter. The dirt-holding capacity of surface filters is limited by the area of the filter surface in contact with the

feedstream. Surface filters tend to be used for feeds with a low solids content and need to be cleaned regularly in order to have a commercially useful performance. The surface removal mechanism is at its most useful in two situations, namely for particles which are quite large, e.g., $>100\text{ }\mu\text{m}$, as for a screen product and for quite small particles, e.g., $<10\text{ }\mu\text{m}$, as for a membrane.

Between these ranges, ie for particle sizes of 10 to $100\text{ }\mu\text{m}$, the depth or gravity or depth filtration mechanism becomes very useful, since products which use this mechanism have a high dirt-holding capacity combined with an acceptable removal efficiency. The granular media filter is the most common example of a device which operates using this type of mechanism to remove particulates from a feedstream (Voutchkov 2010). These filters have a nominal pore size considerably greater than the particles they are capturing. Thus, for a sand filter with a grain size of normally $500\text{ }\mu\text{m}$ (i.e., 0.5 mm) or greater, the nominal pore size of the media is more than $100\text{ }\mu\text{m}$, and there is a wide distribution of channel sizes. In fact, the absolute rating of such a filter will be of the same magnitude as the particles used to form the media bed. However, the bed can routinely capture particles down to $10\text{ }\mu\text{m}$.

The key attribute of the granular media filter is that the pore size at the surface of the bed is much greater than most of the particles in the feed challenge. Particles can therefore enter the media and start to travel with the feed flow through the bed as illustrated in Fig. 1. Potential capture sites are created in the bed wherever particles pass close to a grain of the media. Gravity forces attracting the particle to stick to the surface of a grain overcome the viscous drag forces which would tend to displace the particle from the surface and continue in suspension in the fluid flow.

For small particles, the forces of gravity attraction are relatively weak; hence this type of filtration mechanism is only effective down to a certain particle size, typically around 5 or $10\text{ }\mu\text{m}$. Below that, the gravity attraction forces diminish sharply, reducing by a factor of 1,000 for every order of magnitude (ie factor of 10) reduction in particle size, since the mass is related to the diameter by a cube law.



Granular Media Pretreatment Filtration, Fig. 1 Granular media bed cross section illustrating particle capture mechanism

Due to the depth of the media and the tortuous path created for the feed as it moves through the bed, relatively high removal rates can be achieved, even for particles significantly below the nominal pore size. Media beds of 500 μm sand particles can achieve removal efficiencies of 90–99 % for particles down to 10–20 μm . The nominal rating of the depth filter means that the removal efficiency is variable and is dependent on a host of environmental and operating parameters.

A limitation in this type of device is that large particles can bridge the pores at the surface, creating a cake layer. This effect is known as surface blinding, and if it happens, it prevents the efficient utilization of the pores in the depth of the media, bringing the filtration cycle to a premature end. The surface of the media therefore requires protection with a coarse pretreatment. Typically, a screen with a 300 μm rating is used to prevent blinding.

Although high removal ratings can be achieved for a granular media filter removing particles well

below that of the nominal pore size, the removal efficiency is much lower during the initial ripening period in which the media is “conditioned” by particles in the challenge. The conditioning particles form a fine surface coating on the media which enhances removal. In addition, the filter rating declines toward the end of the cycle as the differential pressure increases across the bed assisting the viscous drag from the fluid flow to dislodge any loosely attached particulates.

Media Characteristics

Media Type

Granular media products can utilize several different media types of different grain sizes and bed depths to form the deep bed filter. The basic media used in the devices include anthracite (a type of coal) and sand, with the additional option of a layer of garnet. It is also quite common to use granular activated carbon (GAC), potentially in addition to anthracite. Anthracite can allow a

biofiltration mechanism to develop in which bacterial colonies supported on the surface of the media consume dissolved organic carbon, thereby improving organic removals. GAC enhances biofiltration characteristics, but note that it can take 4–6 weeks for the bacterial colonies to become fully effective. Generally, the holdup time in the media bed needs to be at least 15 min for biofiltration to be effective.

A contrasting approach is to apply a chlorine residual to the feed to enhance filtration performance and maintain disinfection in the bed. Cl_2 oxidizes a wide range of the contaminants in the feed improving removal efficiencies.

Number of Layers: Single or Multimedia

The simplest granular media filters just use a single type of media, usually sand, but also possibly GAC. A typical rating for such a filter is 20 μm . Standard pretreatment filters use a layer of coarse anthracite followed by a layer of fine sand, the so-called dual media filter (DMF) to provide a 10 μm rating. The media is chosen so that the specific gravity of the upper layer is less than that of the lower layer in order to maintain stratification in long-term use (Wilf 2007).

For finer filtration duties of about 5 μm , a triple media filter can be used in which a final layer of high density garnet provides a polishing step. There are also commercial products using four layers, which allow higher velocities and therefore smaller footprint. Four-layer filters claim to achieve removals down to 1 μm or even lower. Multilayer filters require grains with good sphericity so that the stratification can be maintained after backwashing.

Velocity Range

A single layer filter would tend to use a flow rate of 5–12 m^3/h per m^2 of surface area of the bed, i.e., a linear velocity of 5–12 m/h (2–5 gpm/ft^2). The velocity can be increased with the number of layers and depth of the layers, depending on the degree of removal required. DMF pretreatment plants normally have a velocity of 8–12 m/h . Four-layer filters can be operated at 25–60 m/h , a factor of five times as high as a single media, which reduces footprint significantly.

Polyelectrolyte addition to the feed can also be used to increase velocities, and this is standard practice where footprint is of critical importance, e.g., offshore.

Grain Size Diameter: Coarse Versus Fine

A typical grain diameter can vary from 0.5 mm for a fine bed filter to 1.5 mm for a coarse bed. In a DMF of anthracite and sand, it is common to use an initial layer of coarse anthracite followed by a fine layer of sand to provide a graded bed with finer removal performance nearer the outlet. Higher velocities are used for coarse beds.

Bed Depth: Shallow Versus Deep

The total bed depth of a shallow filter could be around 1 m, whereas a deep bed filter could be from 2.5 to 3.0 m in depth (Voutchkov 2010). An allowance of about 5 % needs to be provided to allow for settlement. For a shallow bed filter treating a good quality feed, a typical DMF bed depth would be 0.5 m of anthracite followed by 0.5 m of sand. A poorer feed quality would require greater depth of up to 1.5 m for each layer. For a filter providing a biofiltration action, a deep bed would be required.

Product Characteristics

Pressure Versus Gravity

A pressure filter encapsulates the media bed in a large pressure vessel, of 2.4 m or up to 3 m in diameter. Although ideally suited for small or medium-sized plants, they are sometimes used for larger plants in which there is an advantage to maintain the pressure head of the feed. Pressure systems also have the advantage of smaller footprint and shorter construction times.

The other type of configuration is the gravity filter in which the media bed is contained in a large tank, potentially made from concrete. Gravity filters are often used where there is no disadvantage in breaking the pressure head of the feed and where the plant layout lends itself to the use of gravity to drive the feed through the bed. Gravity filters are also normally preferred for plants with a high capacity.

Vertical Versus Horizontal

Vertical filters tend to be used for smaller flows, whereas it is more economical to use a horizontal arrangement for higher flow rate. The horizontal configuration can have flow distribution problems during backwash, but this can be overcome by compartmentalizing the vessel, with independent backwashing of each part.

Downflow Versus Upflow

Granular media filters can operate in upflow or downflow configurations, but in a pretreatment context, it is more common for them to be operated with downflow. Downflow has benefits in dealing with algae, since the potential for algal cell rupture is reduced.

Number of Filtration Stages

For a good quality feed, a single-stage DMF would probably be selected, but for a poor quality feed of say >20 NTU, it is common practice to utilize two-stage filtration in which a high rate rapid filter is followed by a slow rate fine bed. Two-stage filtration tends to reduce coagulant use for a given removal. It is quite common to adjust the coagulant dose and/or pH between stages to optimize the overall performance.

Process Sequence

A typical filtration cycle for a granular media filter will be at least 8 h and more probably up to 24 h or even more. Treated water quality will be less good during the ripening period which could last up to 30 min, and some or all of the flow will be wasted or more likely recycled during this period.

After the filtration cycle, a backwash step is carried out. During the backwash step, water passes through the filtration bed in the reverse direction causing bed expansion and removal of deposits. Backwash operation is usually conducted at flow rate of twice the filtration cycle flow, e.g., a typical range of 16–24 m/h for a DMF. Bed expansion during backwash is in the range of 20–50 %. With increased water temperature, the backwash flow rate has to be increased by about 3 % per °C to maintain bed expansion due to lower viscosity of the backwash fluid.

Backwash is mainly conducted with filtered water. In seawater RO plants, RO concentrate is sometimes used for filter backwash to improve recovery. The backwash operation is sometimes combined with air scouring to improve the efficiency of bed expansion and the removal of deposits. Air mixed with backwash water passes through the filtration bed at rate of 55–90 m/h (3–5 scf/ft²-min). Air scouring increases bed expansion and is therefore followed by a high rate water backwash.

The typical backwash sequence takes 3–10 min using an air and water mixture, followed by high rate backwash for 5–10 min. The total backwash volume is typically 2–3 % of the filtrate. Backwash is triggered by a timer with a high differential pressure override.

Process Design

Figure 2 shows a typical process design for a granular media filtration stage in a seawater reverse osmosis (SWRO) desalination duty (Voutchkov 2010).

The pressure drop in a packed bed is related to the velocity of flow through the bed and the characteristics of the media and the feed as shown by the Ergun equation (Richardson et al. 2002). The first term in this equation is dominant for the laminar flow regime and the second becomes dominant for turbulent flow.

Ergun equation:

$$\frac{\Delta P}{L} = \frac{150 V_s \mu (1 - \varepsilon)^2}{D_p^2 \varepsilon^3} + \frac{1.75 V_s^2 \rho (1 - \varepsilon)}{D_p \varepsilon^3}$$

where

Δp is the pressure drop across the bed.

L is the length of the bed.

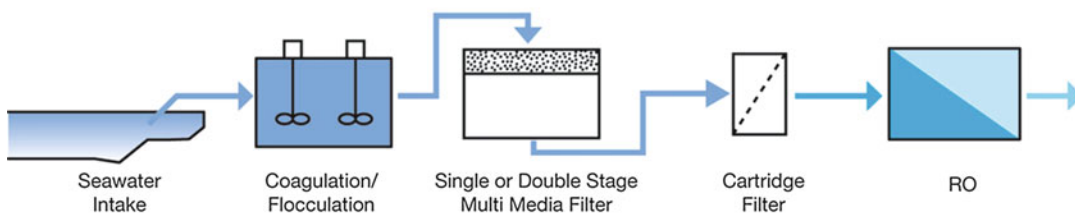
D_p is the equivalent spherical diameter of the packing.

ρ is the density of fluid.

μ is the dynamic viscosity of the fluid.

V_s is the superficial velocity (i.e., the velocity that the fluid would have through the empty tube at the same volumetric flow rate).

ε is the void fraction of the bed (typically 0.6 for sand grains).



Granular Media Pretreatment Filtration, Fig. 2 Conventional RO pretreatment process

The equation applies for a clean bed. As solids are captured from the feed, the characteristics of the bed such as the voidage will change and the pressure drop will rise. Granular media filters have relatively large channels, which means that both lamina and turbulent terms in the equation make important contributions. For media with much finer channels, such as membranes, the flow regime is almost exclusively laminar.

The equation shows that physical characteristics for the bed such as the sphericity of the particles and the voidage between them are important factors in determining pressure drop. In the first term (characteristic for a laminar regime), pressure drop is inversely related to the channel diameter, whereas in the second term (which contributes for a turbulent regime), the pressure drop is inversely related to the channel diameter squared, thus becomes much more important for coarser beds.

Operational Issues

At the start of a filtration cycle, granular media filters normally operate with a low pressure drop. For a shallow bed DMF operated at a moderate rate, the pressure drop will be less than 0.1 bar. During a filtration cycle, the pressure drop will rise to around 0.25 bar. It is important that the pressure drop does not rise too much or channeling may occur in the bed leading to breakthrough. When this happens, the excessive pressure drop causes particle movement in the bed such that low resistance channels open up in low voidage zones of the bed resulting in by-passing. If the particles have good sphericity and are closely packed, it would take a high pressure drop for this to happen, but for

a randomly packed bed formed after expansion during backwash, the bed is prone to this effect.

Channeling can also occur at the vessel walls, and for this reason, the vessel diameter should ideally be 1500 times the mean particle diameter, a criterion which is readily achieved in large-scale commercial units.

A key problem for granular media filters can be biofouling since the extensive surface of the bed can support bacterial colonies which are provided with nutrients from the dissolved organic carbon content (Wilf 2007). Indeed, this action can be intentional and is the basis of biofiltration. The behavior is referred to as biofouling if growth increases to the point that pressure drop becomes excessive. The phenomenon can be controlled by dosing an oxidizing agent such as chlorine, though this might just transfer the biofouling issue to downstream units due to the formation of readily assimilable organic by-products. A strategy to control the problem is to use shock chlorination in which a high chlorine concentration of 5 ppm free residual or more is dosed intermittently, for example, on a daily basis, for a short period of say 30 min.

Filtered Water Quality

Filtrate quality is determined through measurement of turbidity and SDI. There is no defined and consistent correlation between turbidity and SDI. However, field experience indicates that to achieve an SDI below three, the filtrate turbidity has to be below 0.1 NTU, preferably below 0.05 NTU. By choosing an appropriate filtration system design in terms of media type, bed depth, and number of layers, a turbidity of 0.3 NTU can

easily be achieved, and operators target 0.1 NTU or less with a two-stage system.

Dissolved organic carbon (DOC) removal is an important requirement for granular media filtration since this material can cause fouling of downstream RO by direct adsorption and by supporting biofouling. A high level of DOC may increase turbidity and SDI, but there is no simple direct correlation.

Chemical dosing holds the key to achieving low turbidity filtrate, normally using a clarification or flotation stage. A single-stage system usually achieves a modest reduction in DOC of 20–30 %, whereas a two-stage system may achieve 60–70 %. Due to the depth removal mechanism, there will be some degree of variability in the treated water quality achieved as feed quality varies and other seasonal changes occur.

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Graphene Membranes

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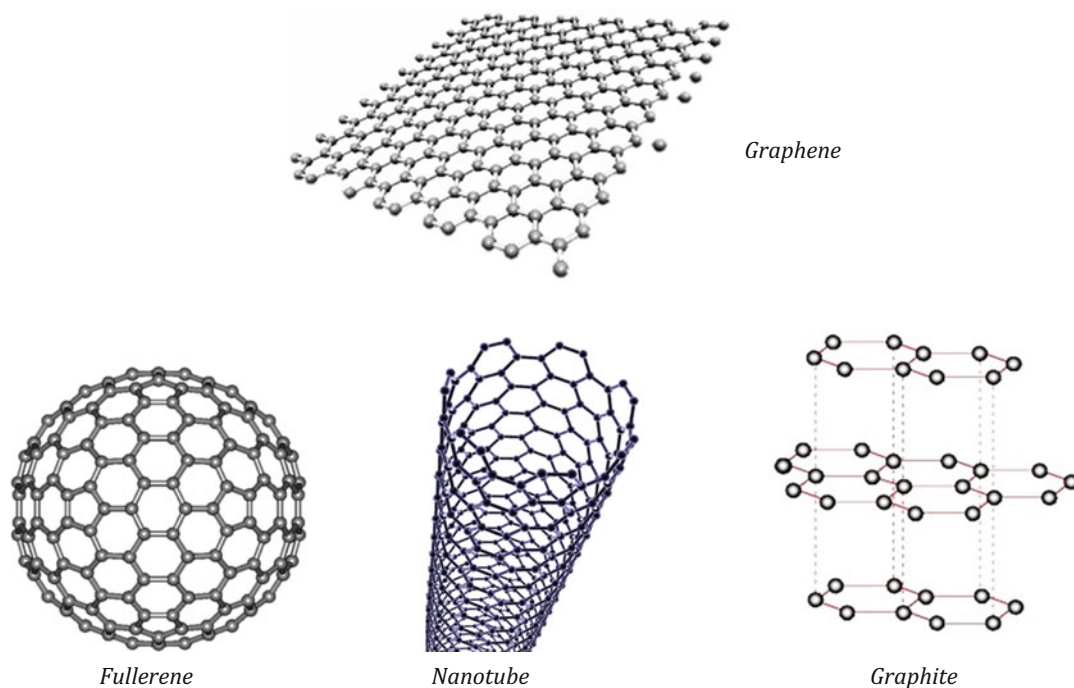
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Among the allotropes of carbon (2D) (Fig. 1), the graphene is one of the most attractive materials

formed by a single layer of sp²-bonded carbon atoms arranged in honeycomb lattice with the atomic thickness of 0.4 nm and a light weight of 0.77 mg/m².

In graphene, the carbon atoms are bonded with three neighboring carbon atoms by planar σ orbitals, which are separated by 120 °C with each other, while pi (π) orbitals are delocalized above and below the graphene sheet (Fig. 2a). Taking into account the electronic configuration of the carbon at the ground state (1s²2s²2p²), the carbon-carbon σ orbitals are covalent bonds deriving from hybridization of the single 2s orbital with two 2p orbitals; these bonds confer robustness and elasticity to the graphene structure. Indeed, a stiffness of 300–400 N/m and a breaking strength of 42 N/m have been estimated for defect-free graphene sheet (Lee et al. 2008). Also, graphene sheets show a spring constant of 1–5 N/m for thickness of 2–8 nm, resulting in a great ability to recover the initial size after strain. These outstanding mechanical properties make undoubtedly the graphene a desirable material for reinforcing objects and devices as well as for the construction of graphene-based nano-electromechanical systems (NEMS) (Bunch 2007).

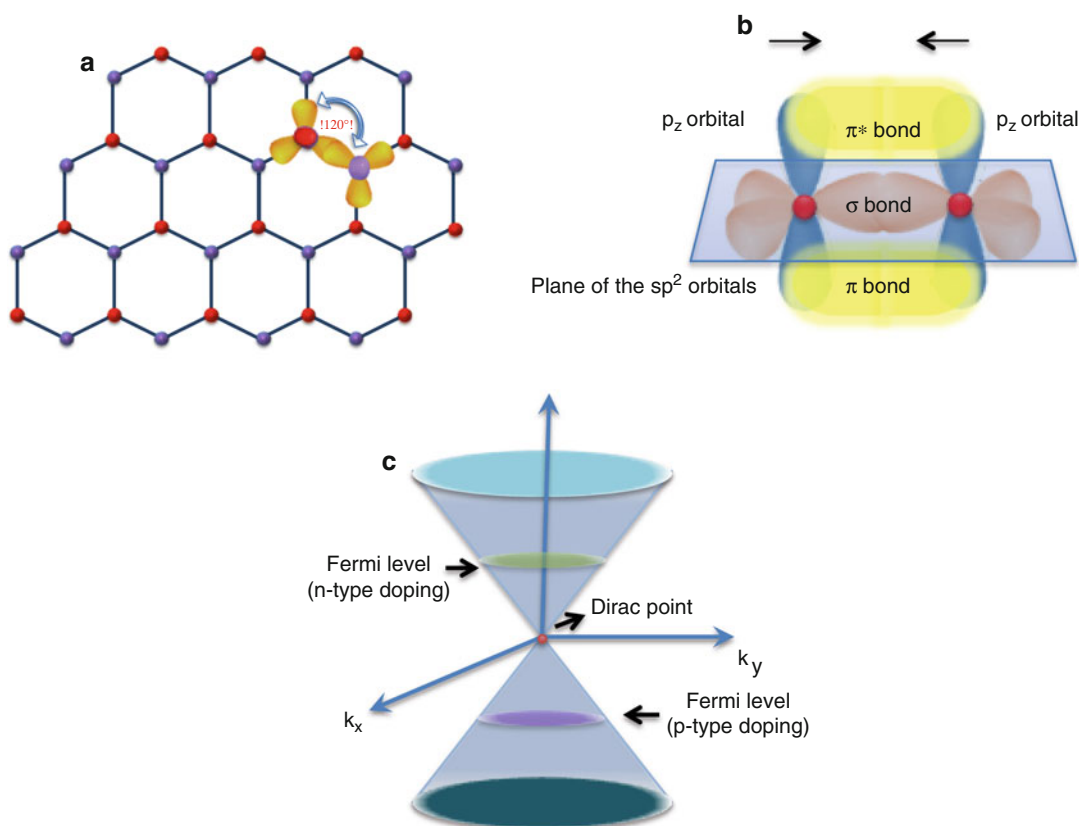
The pi (π) orbitals are instead formed from overlapping of neighboring 2pz perpendicular to the graphene plane (Fig. 2b); the bands π (bonding) and π^* (antibonding) represent the valence band (VB) and the conduction band (CB), respectively, through which the electrons can be delocalized providing excellent electronic properties to the graphene. The mobility of pi (π) electrons is indeed estimated to be 15,000 cm² V⁻¹ s⁻¹ with hypothetical limits of 200,000 cm² V⁻¹ s⁻¹ for free-impurity sheets. Also, the resistivity of the graphene is assessed to be 1.0 10⁻⁸ Ωm at room temperature with a capability of the material to transfer electrical current over 10⁸ Acm⁻². The bands through which the electrons move are represented as two cones touching at the Dirac crossing energy point (Fig. 2c). These two bands, however, degenerate at the corner, the so-called Dirac point or “K” of the hexagonal Brillouin zone, thus resulting in a semimetal with a zero-bandgap due to the



Graphene Membranes, Fig. 1 Carbon allotropes where graphene sheet is the key component: graphene (2), fullerene (0D), nanotubes (1D) and graphite (3D)

identical environment of two carbon atoms located in the unit cell of the graphene lattice (Fig. 2a) (Lau 2012). This could represent a limitation for the use of graphene in electronics, optoelectronics, photonics, bio-sensing, and solar energy harvesting. Nevertheless, the application of an electrical field can induce changes in the Fermi level, thereby causing doping or holes events (Lu 2013). When the Fermi level is above the Dirac point, there are holes in the VB. On the contrary, a predominance of electrons is in the CB when the Fermi level is over the Dirac point. In both the cases, electrons and holes enable the graphene to be transformed from semimetal to semiconductor with much higher conducting properties. This approach, along with the exceptional capability of the “charge carrier” to travel sub-micrometer distances without scattering, opens new horizons and promising perspectives in the development of new approaches for mass production of high-quality semiconducting graphene at low costs.

Currently, the graphene can be produced according to some techniques, including mechanical exfoliation, epitaxial growth, and graphene oxide (Soldano 2010). As always, the choice of each single-manufacturing approach implies advantages and disadvantages, respectively. The mechanical exfoliation takes the advantage to be handled and competitive from the economics point of view, but the technique is not reproducible and reliable enough to be scaled up. The growth of graphene on metallic substrates by chemical vapor deposition (CVD) of hydrocarbons is another possible route for synthesizing single layers of graphene on larger scale, in spite of the high-processing temperatures. However, structural quality and preserved electronic properties represent two important challenges to reach yet. The chemical exfoliation is regarded as a promising scalable and handling approach for mass production of graphene sheets. It relies on the use of reactants in the interspace between graphene layers, thus



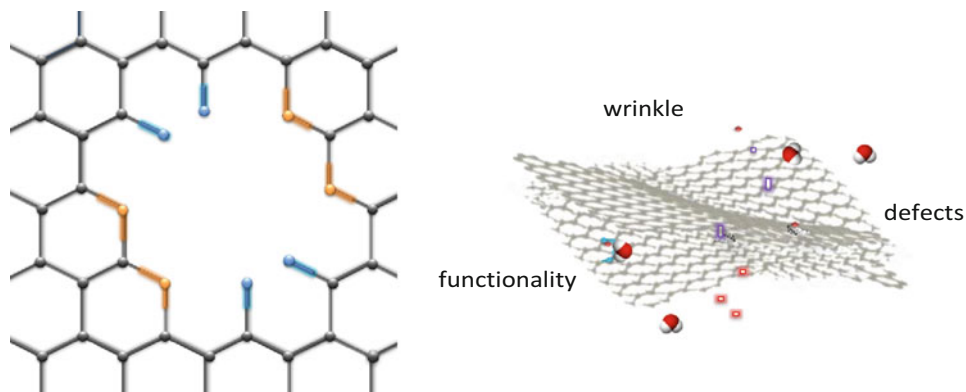
Graphene Membranes, Fig. 2 (a) Honeycomb lattice of graphene with hybridized sp^2 -bonded carbon; (b) delocalized electrons in π (π) orbitals above and below the graphene sheet; (c) the Dirac point or “K” of the hexagonal Brillouin zone

promoting weak interactions such as van der Waals forces and making the exfoliation easier than micromechanical cleavage, wherein cohesive forces between layers and long-distance interactions take place between graphene and substrate. The problem is a partial change in the carbon hybridization from sp^2 to sp^3 due to the oxidation of graphene. The latter is surely an interesting precursor of graphene derivative, but its electronic properties are different from semi-metallic graphene produced according to the other approaches.

However, the use of graphene in membrane separation processes requires some expedients, including controlled nanoporation, modulated layers' inter-distance, and chemical functionalization of the layers, in order to make this already excellent electronic material also an outstanding interface for selective gas separation,

water purification, and (bio)sensors (Xu 2015; Smith 2013; Gugliuzza 2014).

Graphene sheets have been recently proposed as barrier membranes against water and gases for applications in food and pharmaceutical packaging. The related impermeable properties are ascribable to the high density of delocalized electrons, which prevent molecules from passing through the hexagonal rings. Recent density functional theory studies have however demonstrated how the creation of functionalized sub-nanosized holes (around 3 Å) in graphene sheets can enhance the selectivity for the H_2/CH_4 gas pair (Tsetseris and Pantelides 2014). Specifically, values of selectivity of 10^8 for H_2/CH_4 may be obtained through graphene sheets with nitrogen-functionalized pores while selectivity of 10^{23} for H_2/CH_4 by using graphene with all-hydrogen passivated pores (Fig. 3).



Graphene Membranes, Fig. 3 Representative scheme of graphene with functionalized nanopores, defects, and wrinkles responsible for selective behavior

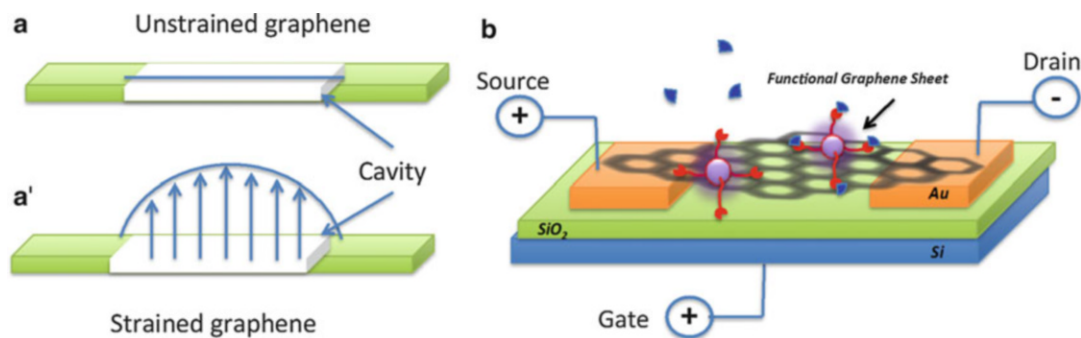
These pores represent a barrier (1.6 eV) for CH_4 , whereas H_2 (0.22 eV) can pass easily. Therefore, the creation of nanoporous in graphene together with the occurrence of local defects and wrinkling and variation of the layer thickness, but also the insertion of functional groups in the pore edges or between the stacked layers, have been simulated to make the graphene selective for gases such as He, Ne, H_2 , CH_4 , and CO_2 (Gadipelli and Guo 2015).

Electron beam, ultraviolet-induced oxidative, etching of holes on graphene surfaces together with the use of molecular building blocks lithography, and tethering of graphene with carbon nanotubes have been proposed to produce nanoporous graphene-based membranes through the deposition of graphene sheets onto substrates, including the polymeric ones. However, it should be better to purify the gas mixtures before passing the pores molded in graphene, since impurities, molecular residues, could obstruct severely the diffusion pathways and affect the selectivity properties. Despite that various predictive studies indicate the nanoporous graphene and derivate such as graphene oxide as excellent materials for gas mixture separation, a lot of academic and industrial research is still necessary to develop on large scale products with suitable structural and chemical fruitful features for scaled applications in gas separation.

Water purification and desalination represent another challenge to reach by using graphene-based membranes as well (Xu 2015). Perforated

graphene with pores of the order of nanometers are big enough to let water pass through, but somewhat small to stop pollutants and salts at the interface. Pore size, layer inter-distance, and functionality together with pore wettability are again parameters to be considered for the optimization of the productivity and efficiency of water purification. Concerning the selectivity of the membrane process, rejection mechanisms based on size exclusion, chemical and electrostatic interactions, and Donnan's exclusion have been proposed. Computational studies concerning, as an example, the separation of NaCl from water have evidenced that small and hydrophobic pores enable at low pressure the rejection of NaCl according to size exclusion mechanisms, while bigger ions in the absence of hydrogen bonding could increase the energy barrier to the ion passage. Ionic exchange mechanisms have been also detected through graphene oxide membranes for the separation of acid from FeCl_3 solutions. The transport of ion H^+ has been estimated to be two orders of magnitude greater than Fe^{3+} ions (Sun 2014).

Some hypotheses of mechanisms for water permeation through graphene and graphene oxide membranes have been also suggested, including capillary-driven flow between a water monolayer and the pristine graphene layer and passage through porous microfractures formed in the graphene sheets. The latter have been envisaged as critical elements for enhancing water permeation, while hydrophilic groups attached to the



Graphene Membranes, Fig. 4 Scheme of an unstrained (a) and strain (a') graphene layer over a cavity. Scheme of a functional graphene sensor-based device (b)

graphene oxide have been regarded as responsible for slowing down the flux due to the establishment of hydrogen bonding between water and oxidized regions of graphene. On this basis, well-sized interlayer gaps and broader nanochannels through graphene or graphene oxide are expected to well retain salt ions and undesired organic compounds, while the water permeation is expected to increase over three orders of magnitude with respect to traditional commercial reverse osmosis membranes.

Undoubtedly, membranes prepared from perforated and functionalized graphene represent an attractive solution to the incessant requirement of highly performing gas and liquid separations. The outstanding mechanical properties together with the predicted ultrafast permeance and high-retention power make this class of membranes promising candidates for gas separation and water purification processes. However, a lot of explorative research is required to optimize mass production of high-quality, durable, and energy-efficient graphene wherein the formation of nanopores and the insertion of functional moieties between the stacked layers can be perfectly controlled in number, shape, and size without yielding mechanically vulnerable points. Also, the resistance of this kind of materials to swelling and fouling and ion clogging, which often take place during separation processes, needs to be detected as well as the ability to work under high pressure and harsh conditions. It is auspicious that computational and experimental studies can be reciprocally validated, thus casting new light on predominant transport mechanisms. In this way,

the design of well-defined structure can be addressed at overcoming the performance of traditional membrane separations on larger scale.

Theoretical and experimental studies have also confirmed the high potential of graphene for nanoelectromechanical system (NEMS) applications, where electrical conduction and outstanding mechanical and optical properties (i.e., a transparency with a transmittance that changes from 95 % to 70 % for thickness ranging from 2 to 10 nm with an absorption of 2.3 % of white light) can be combined (Bunch 2007). As an example, graphene sheets exhibit a pressure sensitivity of two- to tenfolds superior to the standard silicon- or carbon nanotube-based micro-electromechanical sensors (MEMSs). Despite that graphene has no band gap, such the piezoelectrical properties cause changes in the electronic structure under strain (up to 23 %) resulting in a shift of the Fermi level (Smith 2013). When used as pressure sensors, freely suspended graphene membranes can sense a gradient of pressure established between the external surrounding atmosphere and the unchanged internal environment, which is regarded as the result of no permeability of graphene sheet to air. This gradient of pressure yields a proportional force, thus causing the expansion of graphene and, consequently, a variation of the resistance with enhancing of the electrical charge transfer (Figs 4a-a'). This ability of the graphene membranes makes them extremely promising materials for controlling and monitoring actions in the field of automobile, aerospace, textiles, and weather.

Despite those proof-of-concept demonstrations (Fig. 4b), graphene membranes have been also proposed as chemical (e.g., small organic compounds and ions) and biological (e.g., sugars, proteins, DNAs) sensors enabling to reveal an increase in the current passage as an effect of doping generated by interactions between the functional graphene sheet and specific analyte (Liu 2012). As a chemical sensor, a recent membrane integrated with single-walled carbon nanotubes, which are regarded as rolled graphene sheets, has been proposed for detection and regulation of surrounding humid atmosphere (Pingitore 2015). Graphene membranes are expected to have enhanced performance.

Similarly to gas and water separation, a deeper understanding of the mechanisms which regulate recognition and interactions and signal transmission are necessary in order to promote technology transfer and commercial application of devices realized according to reliable, reproducible, and scalable manufacturing processes.

Overall, the use of graphene could lead to a completely novel membrane with well-organized ultrathin nanocomposite architecture. They may promote very high selectivity thanks to precise pore morphology control as well as high permeability thanks to a very thin layer. Furthermore, energy use can be minimized, thanks to facilitated transport promoted through the membrane by favorable surface interactions.

Production of ultrathin nanocomposite membranes is challenging to produce, and therefore, it is difficult to predict the real commercial promise. However, the importance of energy reduction in massive production, such as seawater desalination, provides a crucial driver, which will foster the development of these novel membranes.

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H₂ Permeation Through Pd-Based Membranes

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Synonyms

Hydrogen permeation

Palladium is known to be one of the most effective metals for hydrogen adsorption, dissociation, and recombination even though the permeability of this metal is by an order of magnitude lower than that of refractory metals such as tantalum, vanadium, and niobium.

In 1863, Sainte-Claire Deville and Troost discovered that hydrogen is able to permeate through palladium; later, in 1866, Graham found that palladium can absorb huge amounts of hydrogen (several times with respect to its initial volume) at room temperature. The palladium-based membrane technology for hydrogen production has come into life in the late 1950s. In the 1960s, pioneering studies by Gryaznov led to the development of a breakthrough membrane reactor when palladium-based membranes were

used for hydrogen supply or withdrawal from the reaction zone, thus providing improved yield and high catalyst effectiveness (Pagliery and Way 2002).

Hydrogen permeation through solid palladium proceeds via the solution–diffusion mechanism, and this mechanism involves the following steps: (a) diffusion of molecular hydrogen to the surface of the palladium-based membrane, (b) a reversible dissociative adsorption on the palladium surface, (c) dissolution of atomic hydrogen in the bulk metal, (d) diffusion of atomic hydrogen through the bulk metal, (e) association of hydrogen atom on the palladium surface, (f) desorption of molecular hydrogen from the surface, and (g) diffusion of molecular hydrogen away from the surface (Yun and Oyama 2011). On the palladium surfaces, the dissociative adsorption of hydrogen molecules proceeds with a low or zero activation energy barrier. This is the first step in bulk absorption toward the formation of metal hydrides.

Generally, hydrogen permeation is described by the following equation:

$$J = P(p_h^n - p_l^n)/L,$$

where J is the hydrogen flux, P is the permeability coefficient, L is the thickness of the palladium layer, p_h and p_l are the partial pressures of hydrogen on the high-pressure (feed) side and the

low-pressure (permeate) side, respectively, and n is the pressure exponent. This exponent generally ranges from 0.5 to 1 depending on the rate-controlling step [steps (a–g)]. According to Sievert's law, when the rate-controlling step is the bulk diffusion through the palladium layer [step (c)], the n value is equal to 0.5 because the diffusion rate is proportional to the concentration of hydrogen atoms on the opposite sides of the metal surface and this hydrogen concentration is proportional to the square root of the hydrogen pressure. When mass transport to or from the surface (a, g) or dissociative adsorption (b) or associative desorption (e) becomes rate-controlling steps, the expected value of n is 1 because these processes depend linearly on the concentration of molecular hydrogen. In the case of the Pd-based composite membranes with thick ($>5\ \mu\text{m}$) Pd layers, the n values are higher than 0.5, and this fact can be explained by defects or pinholes through which substantial amounts of hydrogen can permeate. This process proceeds via the Knudsen or Poiseuille flow mechanisms, and the corresponding exponents are higher than 0.5.

In the case of binary palladium alloys, hydrogen permeation is generally proportional to the average bond distance of the alloys. Permeability is the product of diffusivity and solubility. In the case of Pd–Ag alloys, hydrogen solubility increases with increasing Ag content up to 20–40 wt.%; hydrogen diffusivity decreases with increasing Ag content. Concomitant changes in solubility and diffusivity lead to higher hydrogen permeability (1.7 times higher) as compared with that of pure Pd at 23 wt.% of Ag and at 623K (Ma et al. 2003).

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Hairy Superhydrophobic Surface

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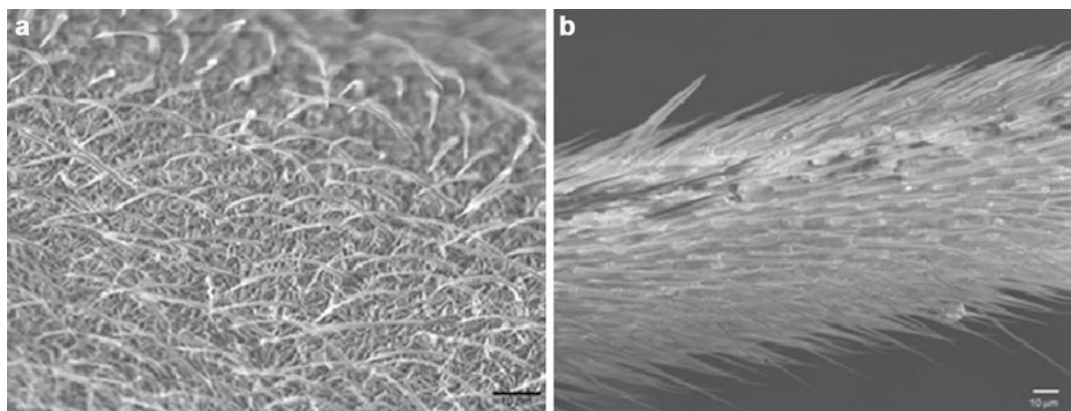
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Superhydrophobicity not only exists on lotus-like leaves but also on surfaces comprising high-aspect ratio soft hairs. Although the piliferous exterior is found in almost all water-repellent arthropods and has been noted for over 100 years, (Comstock 1887) compared to the Lotus effect, studies based on this structure are relatively limited. The superhydrophobicity is dominated by both surface roughness and chemistry, so as the hairy superhydrophobic surfaces. Surface roughness arises from the arrangement of hairs, and, similar to the water-repellent leaves, hairs are also covered with a layer of epicuticular wax that renders the exterior hydrophobic and prevents the penetration of water. The wax layer is not only important in water repellency but also in water retention within the insect's structure; removal of the waxy layer will result in rapid desiccation of the insects (Wigglesworth 1945).

The hairs in almost all water-repellent arthropods are generally arranged as a series of “I” shapes. Most of the hairs are not only inclined but curled with their tips parallel to the bodies, which in turn provides a greater resistance to wetting. The array of tilted pillars increases the pressure required to penetrate into the grooves, as the free space between the tilted pillars is reduced, making them favorable to resisting water. A horizontal array of cylindrical pillars also provides a greater water resistance (Extrand 2002). Overall, a series of inclined and parallel pillar arrays is energetically unfavorable for a liquid to intrude between the pillars parallel to the interface.

Figure 1 shows an example of typical hairy superhydrophobic surface, water strider's body and its leg (Hsu 2010). Two different sets of

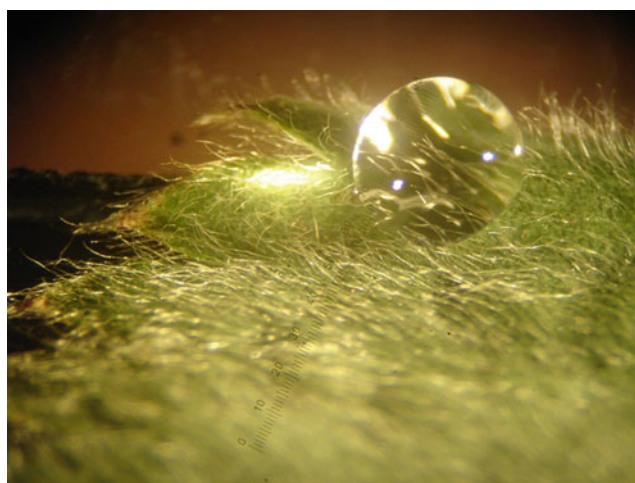


Hairy Superhydrophobic Surface, Fig. 1 SEM images of the hair layer of the water strider's body. The hair tips are bent inward toward the body to enhance the degree of

water repellency. (a) The hair on strider's abdomen is tilted at around $30\text{--}45^\circ$ relative to the body surface. (b) The hair on strider's leg (Hsu 2010)

H

Hairy Superhydrophobic Surface, Fig. 2 A water droplet forms a spherical bead on Lady's Mantle leaf



body hair can be usually found from the arthropods. Longer hairs, termed macrotrichia, are less dense with lengths of 20 mm and diameters of around 1 mm, and shorter hairs, termed microtrichia, are approximately 2 mm long and 100 nm wide. Longer hairs taper to a point from the base and incline at an angle of $30\text{--}45^\circ$ with their tips parallel to the body surface. Shorter hairs are however highly dense and are more randomly oriented. The hair is also patterned with nanoscaled grooves with widths of around 400 nm, thus providing a structure with hierarchical roughness. Many arthropods possessing hairy integument are reported to have contact angles

reaching over 160° , and it provides crucial living functions for the species, such as underwater respiration, walking on water, or surviving under rain impact (Bush et al. 2008). More details on underwater respiration can be found in the section of plastron effect.

Hairy leaves with a feature similar to *lotus effect* are also common. These plants, i.e., Lady's Mantle (*Alchemilla vulgaris*), exhibit a plurality of flexible hairs, termed trichomes, on their leaves and stems (Fig. 2). Water droplets on the fuzzy leaves can be suspended by the trichomes, which effectively prevent the droplets from wetting the leaf. Although the leaf itself

shows an excellent hydrophobicity, those trichomes are found to be hydrophilic (Otten and Herminghaus 2004). Water droplets are pinned by the hydrophilic trichomes causing high contact angle but roll-off angle.

Cross-References

- Lotus Effect
- Plastron Effect
- Young's Model

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Halar

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Halar[®] ECTFE (ethylene chlorotrifluoroethylene) is a semicrystalline fluoropolymer based on ethylene and chlorotrifluoroethylene. It is currently utilized in several demanding market segments where high purity, outstanding resistance to harsh environments, low permeation, and high temperature stability are needed. Examples of applications are chemical processing, semiconductors, wire and cable, and the pharmaceutical industry.

Meltblown filters made by Halar[®] ECTFE are commercially available for pharmaceutical applications, solvent filtration, and semiconductor applications where high ozone resistance is needed. Other possible applications of Halar[®] ECTFE membranes are membrane contactors, including membrane distillation, pervaporation, and industrial water treatment.

The following features make Halar[®] ECTFE a suitable material for manufacturing membranes for specialty applications:

- Stability at pH levels ranging from 1 to 14
- Outstanding resistance to organic solvents, ozone, and chlorine
- Very good tensile properties
- High temperature stability – continuous use up to 150 °C
- Melt processability, including TIPS (thermally induced phase separation) technology for membrane manufacturing
- Low level of extractible
- FDA compliance for selected grades

The general physical properties of the Halar[®] ECTFE grades available for membrane applications are shown in Table 1.

Because of its exceptional chemical resistance, Halar[®] ECTFE cannot be processed via solution phase inversion. It must be processed at temperatures close to its melting point (200–240 °C) using a TIPS process for manufacturing hollow fiber and flat sheet membranes. Typical diluents used to process this material are high boiling solvents such as acetyl tributyl citrate, glycerol triacetate (GTA), dibutyl phthalate (DBP), and dioctyl phthalate (DOP) (Simone et al. 2012). The polymer should be melt blended with the selected solvent, casted or extruded into the desired form, and cooled at a temperature that promotes phase separation. As final step the diluent should be extracted from the membrane, typically with a low boiling solvent that is mixable with the diluent.

Phase diagrams of Halar[®] ECTFE are available in the literature (Ramaswamy et al. 2002), together with examples of processing for manufacturing membranes and membrane properties (Roh et al. 2010). For example, when using

Halar, Table 1 General physical properties of Halar[®] ECTFE commercial grades

Halar [®] grade	Melting point	Melt flow index	Tensile modulus	Contact angle
	Tm (°C)	g/10 min at 275 °C	MPa	
Halar 901	242	1 @ 2.16 kg	1,600–1,800	90–95°
Halar 902	222	1 @ 5 kg	1,600–1,800	90–95°

DBP as solvent, it is possible to obtain a liquid-liquid demixing for polymer concentrations below 25 % and solid-liquid demixing with polymer crystallization for polymer content above 25 %. It is possible as well to extend the liquid-liquid demixing region of the phase diagram by changing the polarity of solvent, for instance by adding a non-solvent in the polymer mixture.

It is possible to manufacture either flat sheet either hollow fiber membranes with Halar[®] ECTFE. The equipment must be properly designed taking into consideration the needed processing temperature; its corrosion resistance in contact with fluoropolymers must be verified before use.

Porosity of membrane can vary from MF to UF according to processing parameters, such as polymer concentration, type of solvent, processing temperature, air gap, and cooling rate; it is possible as well to obtain symmetrical or asymmetrical structures and to fine tune the thickness of the skin layer (Müller 2006).

Halar[®] ECTFE is a hydrophobic material due to its chemical composition. Surface properties can be modified with posttreatments that are typically performed at industrial level for obtaining desired performances of the finished membranes.

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Halophiles

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Halophiles (i.e., “salt loving”) are organisms that live in high salt concentrations. In taxonomy most of them belong to the Archaea kingdom, but also *Halobacteria* and some Eukarya were isolated. Often they are colored orange, red, or pink/purple; colonies are evidencing the presence of carotenoids and bacteriorhodopsin. The latter is used to absorb light, which provides energy to create ATP. *Halobacteria* also possess a second pigment, halorhodopsin, which pumps chloride ions in the cell in response to photons, creating a voltage gradient and assisting in the production of energy from light. A number of species have been isolated in oceans but also in environment with salt concentration much higher than marine ones like in salty lakes (e.g., Dead Sea) or in evaporation ponds. Halophiles, both aerobes and anaerobes, may use a variety of nutrients and energy sources. Anaerobic ones include phototrophic, fermentative, sulfate-reducing, homoacetogenic, and methanogenic species. Halophiles require NaCl for growth, while halotolerant organisms can stand saline conditions up to 0.8 M NaCl, moderate halophiles prefer salt concentration in the range 0.8–3.4 M, and finally extreme halophiles grow at higher concentrations up to 5.1 M NaCl (Oren 2002a). These microorganisms have evolved physiological and genetic characteristics to cope with the increase in osmotic pressure in different ways. The extremely halophilic Archaea accumulate ions such as K⁺; other bacteria developed biosynthetic pathways to synthesized

compatible solutes (e.g., glycine, betaine, sugars, polyols, amino acids, and ectoines) in high concentration so as to make the cytoplasm isotonic with respect to the surrounding medium; besides, they often present efficient ion pumps, UV-absorbing pigments, and acidic proteins, which help them to resist the osmotic stress and the denaturing effects of salts, as well as intense solar radiation. Many of these characteristics constitute valuable resources for biotechnology and nanotechnology (Oren 2002b). Salty food bioprocessing and fermentation (such as soy sauce, Chinese fermented beans, salted cod, salted anchovies, sauerkraut, etc.) often involve *Halobacteria*, as either essential ingredients or accidental contaminants. Besides these food applications, compatible solutes, which are small biomolecules that also help to protect cells against stresses like high temperature, desiccation, and freezing, have now been used for 15 years in cosmeceutical products. These peculiarities improved performances of moisturizers and other products, thus prompting the research on bioprocess improvement. Recently, using ectoine-excreting strain *Halomonas salina* DSM 5928(T), a new process was developed by Lang and co-authors (2011) for high-efficiency production of ectoine, which involved a combined process of batch fermentation to grow cells followed by a resting cell production phase. Hydroxyectoines were efficiently produced using a microfiltration membrane bioreactor (Schiraldi et al. 2006). More recently also the production of mannosylglycerate (MG) was established through the milking process. In particular the trehalose-deficient mutant of the strain *Thermus thermophilus* RQ-1 was cultivated using upshock fermentation and osmotic downshock, for the effective production/excretion of MG. More than 90 % of the intracellularly accumulated solute was recovered from the water fraction. Although currently established applications of halophiles are limited primarily to compatible solutes in the cosmetic industry and carotene and hydrolases in the nutritional and food industries, many other novel applications are under development. They include specialized applications for films of bacteriorhodopsin from halophiles for a variety of optical

nanodevices, including high-capacity computer storage; some subcellular components, such as polyhydroxyalkanoate granules, gas vesicles, and phospholipid vesicles, and bioactive compounds like halocins are being developed for medical applications. Last but not least, important metabolic activities of halophiles have also been tapped for a variety of environmental applications and specifically for bioremediation of pollutants in saline wastewaters.

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Heat and Mass Transfer in Membrane Distillation

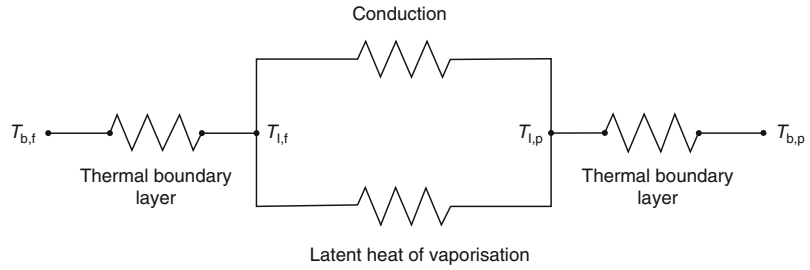
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Membrane distillation (MD) is a membrane separation process based on the principle of evaporation which uses hydrophobic membrane as separating medium. Unlike the membrane process of ultrafiltration (UF) and reverse osmosis (RO) which only contain mass transfer, MD also contains heat transfer and the heat transfer is a key factor affecting mass transfer efficiency. So the investigation of heat and mass transfer in MD process is the key to explore the mechanism of MD process. Many scientists have made

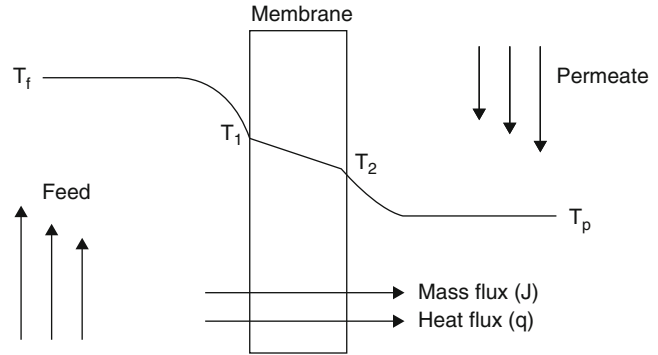
Heat and Mass Transfer in Membrane

Distillation, Fig. 1 Heat transfer resistances in membrane distillation



Heat and Mass Transfer in Membrane

Distillation, Fig. 2 Direct contact membrane distillation



significant progress in the study of heat and mass transfer in MD process.

Heat Transfer

The heat transfer of MD consists of three steps, as shown in Fig. 1. First, heat transfer by the way of convection in the feed boundary layer. Second, heat transfer by the way of conduction through the membrane and the heat flows together with the vapor through the membrane pores, i.e., the latent heat of vaporization. Third, heat transfer by the way of convection in the permeate boundary layer. All types of MD contain the first two steps, while for the third step, other types of MD do not contain it except DCMD.

At steady state, the overall heat transfer coefficient (H) of the MD process can be expressed by a resistance in series model (M. Khayet et al. 2000):

$$\frac{1}{H} = \frac{1}{h_f} + \frac{1}{h_m + J\Delta H_v / \Delta T_m} + \frac{1}{h_p}$$

where h_f , h_m , and h_p are the individual heat transfer coefficients of liquid feed phase, membrane,

and permeate, respectively; ΔH_v is the heat of vaporization and ΔT_m is the temperature drop across the membrane.

For MD process, heat and mass transfer occur simultaneously and result in complex heat transfer mechanisms. So the mass transfer can affect both heat transfer rates and heat transfer coefficients. The heat transfer model has been proposed to describe the heat transfer mechanisms in MD and facilitates the evaluation of the membrane surface temperatures. In most literatures, the heat transfer model for MD was developed based on the assumption of linear temperature profile and isenthalpy flow of vapor (Figs. 2, 3, and 4).

The effective energy transferring from the feed bulk to the membrane surface is:

$$Q_f = h_f(T_f - T_{fm})$$

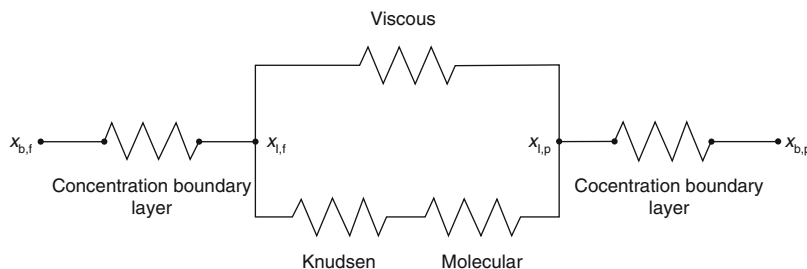
The energy transferring across the membrane is:

$$Q_m = J\Delta H + \frac{h_m}{\delta}(T_{fm} - T_{pm})$$

For the VMD process, the contribution of heat conduction in the membrane matrix

Heat and Mass Transfer in Membrane

Distillation, Fig. 5 Mass transfer resistances in membrane distillation



membrane and high operating temperature as well (Phattaranawik and Jiraratananon 2001). Moreover, the heat transfer by convection is ignored in the MD process, except in AGMD (Curcio and Drioli 2005).

Mass Transfer

The mass flux (J) in MD process is assumed to be proportional to the vapor pressure difference across the membrane and is given by:

$$J = C_m(P_f - P_p)$$

where C_m is the membrane coefficient, P_f and P_p are the vapor pressure at the membrane feed and permeate surfaces, which can be calculated from the Antoine equation (Fig. 5). For different types of MD processes, the obtainment of C_m is based on different models:

For DCMD process, mass transfer through the membrane can be divided into three models. These models relate the mass transport with collisions between molecules, and/or molecules with membrane. Knudsen diffusion takes place when the pore size is too small, such that the collision between the molecules and the inside walls of the membrane suitably expresses the mass transport and the collision between molecules can be ignored (Zhongwei et al. 2003). Molecular diffusion occurs when the molecules move corresponding to each other under the influence of concentration gradients. In Poiseuille flow (viscous flow), the gas molecules act as a continuous fluid driven by a pressure gradient.

In AGMD process, the molecular diffusion theory is used to describe the transfer of vapor molecules through the membrane and the air gap. A stagnant gas film (air) is assumed to lie inside the membrane at the air gap side.

For VMD process, in order to remove air trapped in the membrane pores, the deaeration of the feed solution or a continuous vacuum in the permeate side should be applied. Consequently, the ordinary molecular diffusion resistance is neglected. The Knudsen mechanism is used to express the mass transfer (Bandini and Sarti 1999), Poiseuille flow, or both together (Banat and Simandl 1994).

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Heavy Metal Recovery by Chelating Agents and Membranes

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Heavy metal concentration from wastewaters can be carried out by several membrane operations. Electrodialysis (ED), reversed osmosis (RO), and nanofiltration (NF) membranes retain polyvalent cations. Alternatively, heavy metals can be concentrated by polymer-enhanced ultrafiltration (PEUF) as well.

Further, membrane separations, combined with other process, can contribute to heavy metal recovery from groundwater, contaminated soils, sediments, sludge, etc (Dermont et al. 2008; Hashim et al. 2011; Tsang et al. 2012). First of all, heavy metals must be extracted from the solid matrix using a washing solution containing a suitable extractant. The huge amount of metal-containing solution produced can be concentrated by membrane technologies with the concomitant production of a clean permeate solution, which ideally should be reused.

Metal extraction efficiency depends on several factors such as extractant/metal affinity, extractant/metal ratio, leaching method, liquid/solid ratio, pH, and extraction time. Heavy metal extraction has mainly been done by solutions of strong acids, chelating agents, dendrimers, surfactants, or reducing or oxidizing agents (Dermont et al. 2008). All of them but acid extraction takes place under mild conditions preventing structural changes in the matrix to be decontaminated.

The most used chelating agents are EDTA (ethylenediaminetetracetic), NTA (nitrilotriacetic acid), and DTPA (diethylenetriaminepentaacetic acid). They form very stable chelates and they are very efficient in removing heavy metal ions bound to mineral and organic fraction of soil (Hashim et al. 2011). One of their drawbacks is their low selectivity, which involves high reagent consumption due to the complexation of Ca and

Fe. Further, they show a low biodegradability, and biodegradable chelating agents such as EDDS ([S,S]-ethylenediaminedisuccinic acid), IDSA (iminodisuccinic acid), MGDA (methylglycinediacetic acid), and citric acid have been receiving increasing attention in recent years.

Because of their molecular size, chelates can be concentrated by nanofiltration, but previously, colloids that can clog the NF membranes have to be removed by microfiltration or ultrafiltration. Recycling the chelating agent improves the economical competitiveness of the process and diminishes the environmental impact, especially for nonbiodegradable chelating agents. That involves separating metal and ligand in the contaminated washing solution. Ion exchange resins and selective precipitation of metal or chelating agents by addition of chemical agents have been proposed. Experiments at laboratory scale have showed that some NF membranes are able to reject Cu^{2+} while citric acid leaks. That can be achieved in acidic conditions when the chelate is broken and NF membrane is positively charged, which favors the rejection of Cu^{2+} cations and the leakage of neutral or slightly negatively charged citric acid.

Some water-soluble polymers contain ligand groups that can form chelates with heavy metals as well. They can be retained by ultrafiltration membranes. At low pH, metal ions are released from the polymer and a new ultrafiltration operation allows one to separate them. The polymer can be regenerated by alkali addition and reused. This process is named polymer-enhanced ultrafiltration (PEUF). Recently, dendrimers, highly branched macromolecular compounds with suitable terminal functional groups, have been tested for heavy metal recovery from contaminated soil.

Cross-References

- ▶ [Heavy Metal Recovery by Membrane Operations](#)
- ▶ [Heavy Metal Recovery by Polymer-Enhanced UF](#)
- ▶ [Nanofiltration](#)
- ▶ [Ultrafiltration \(UF\)](#)

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Heavy Metal Recovery by Membrane Operations

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Several industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries, pesticides, etc., produce heavy metal (Cd, Cr, Cu, Hg, Ni, Pb, Zn) wastewaters. Heavy metals are not biodegradable and persist in the environment: waters, soils, sediments, etc. Further, their recovery could be attractive from the economical perspective, and several technologies have been studied and proposed to carry it out: chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation-flocculation, flotation, and electrochemical methods (Coman et al. 2013; Fu and Wang 2011; Kurniawan et al. 2006). Membrane separation technologies yield a high efficiency and allow continuous operation. However, to prevent membrane clog, a pretreatment of the polluted effluent to achieve a clean feed is required. Further, they need careful operation and periodic washing to prevent membrane damages and fouling.

Membrane separations can reduce the volume of contaminated water, making the next processes necessary to full recovery easier and cheaper. At the same time, a clean permeate that meets the applicable effluent guidelines is obtained. That

can be achieved with high efficiency using various membrane technologies: ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) (Coman et al. 2013; Fu and Wang 2011; Kurniawan et al. 2006).

UF membranes reject macromolecules, but their pores are not small enough to retain heavy metal ions such as Cd^{2+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Ni^{3+} , etc. Nevertheless, they can be concentrated with the addition of a soluble polymer or surfactant that binds the metal ions. Those processes are named polymer-enhanced ultrafiltration (PEUF) and surfactant-enhanced ultrafiltration (SEUF) (Coman et al. 2013; Fu and Wang 2011; Kurniawan et al. 2006). At low pH, metal ions are released from the polymer and a new ultrafiltration operation allows one to separate them. The polymer can be regenerated by alkali addition and reused.

RO is used to remove almost everything from the water which includes small molecules and ions. It can produce drinking water from brackish water or seawater. Therefore, it has been shown to concentrate heavy metal ions such as Cd^{2+} , Cu^{2+} , and Ni^{2+} . However, compared to other membrane technologies, RO requires the highest pressure and energy cost.

Nanofiltration (NF) is the intermediate process between UF and RO (Soldenhoff et al. 2005). NF membranes usually have an electrical charge, positive for pH values lower than the membrane isoelectric point (IEP) and negative for higher pH values. NF yields high rejections of heavy metal ions, although NF membrane pores are larger than heavy metal ions in solution. That is due to the contribution to the separation process of several mechanisms: steric (sieving), electric (Donan), and dielectric (born and image forces). Dielectric and Donan effects strongly favor the rejection of polyvalent ions. That makes NF very suitable for heavy metal concentration, which can be done in one step and at lower pressure and energy cost than RO.

Electrodialysis (ED) is another membrane process for the separation of ions that uses an electric field as the driving force. It is an alternative to RO for the production of drinking water. It has been demonstrated to be able to concentrate hexavalent

and trivalent chromium and Cd^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , and Fe^{3+} .

Membrane technologies can contribute to the heavy metal recovery from contaminated underground water, soils, sediments, sludge, etc. However, a previous extraction of metals is needed, which can be achieved with acids, chelating agents, dendrimers, or surfactants.

Cross-References

- [Electrodialysis](#)
- [Heavy Metal Recovery by Chelating Agents and Membranes](#)
- [Heavy Metal Recovery by Polymer-Enhanced UF](#)
- [Nanofiltration](#)
- [Ultrafiltration \(UF\)](#)

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Heavy Metal Recovery by Polymer-Enhanced UF

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Polymer-enhanced ultrafiltration (PEUF) is one of the membrane operations that can be used to separate or concentrate heavy metal from

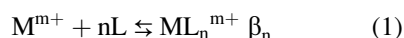
liquid streams. It is also called polymer-assisted ultrafiltration (PAF), complexation-ultrafiltration process (CUFP), or polymer-supported ultrafiltration (PSU) (Rivas et al. 2009).

Ultrafiltration membranes reject macromolecules, but their pores are not small enough to retain heavy metal ions such as Cd^{2+} , Cu^{2+} , Ni^{2+} , Ni^{3+} , Hg^{2+} , etc. Nevertheless, if a soluble polymer able of binding polyvalent cations is added to a solution containing heavy metal ions (F), the resulting metal-polymer complex will be retained by UF membranes. Then, a clean permeate (P) can be obtained and the heavy metals will be concentrated in the retentate stream (R). See figure 1.

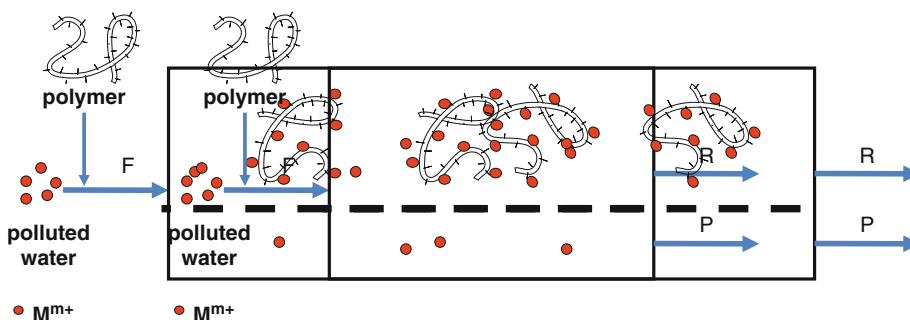
The polymers contain functional groups such as amine, carboxylated, phosphonic, or sulfonate which link to metals either through ionic or chelating bonds. The most used synthetic polymers are polyacrylic acid (PAA) and polyethyleneimine (PEI) (Rivas et al. 2009). The use of natural polymers (chitosan, humic acids, etc.) and polymers anchored on the membrane represents growing alternatives.

A suitable polymer should have a high affinity for target ions and should be able to be recycled in order to make the process economically feasible. It should be biodegradable to prevent new environmental problems, but it cannot have a very short half-life in working conditions. As commercial or natural polymers have a molecular weight distribution, they must previously undergo a diafiltration process to remove short chains, which would bind heavy metals but would leak through the UF membrane. Further, its interactions with membrane materials should be considered to minimize fouling.

Modeling PEUF has usually been carried out through the classic complexation (or exchange ions) equilibrium reactions. For instance, the union between a heavy metal ion, M^{m+} , and a neutral ligand group of the polymer, L, can be represented by the following chemical equilibriums and their respective constants:

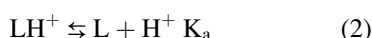


For $n=1, 2, 3, \dots$



Heavy Metal Recovery by Polymer-Enhanced UF, Fig. 1 Scheme of PEUF. (F: feed, R: retentate, P: permeate).

The protonation of the L group is described by:



High values of β_n indicate a strong affinity between polymer and target ion. Generally, the basic forms of ligands ($R-COO^-$, $R-NH_2$, etc.) bind the metal ions, but the acid forms ($R-COOH$, $R-NH_3^+$, etc.) do not do it. This fact can be used for polymer recycling. When an acid is added to the metal-polymer complex solution, metal ions are shifted by protons from the ligand sites. A second ultrafiltration operation yields to a permeate containing free heavy metal ions and a retentate with polymer. The polymer can be regenerated by the alkali addition and therefore reused. The global process requires the consumption of an acid and an alkali, and it is a concentration operation as the permeate in acid medium contains most of the heavy metal from the initial contaminated water, but in a smaller volume.

Nanofiltration and reverse osmosis membranes are able to retain and therefore concentrate heavy metal ions without the need of chemical addition. Nevertheless, they require higher pressures and energy consumption than UF. Selectivity is an additional advantage of PEUF as β_n values are particular for any metal-polymer pair.

Micellar-enhanced ultrafiltration (MEUF) is a similar process to PEUF. Instead of a polymer, a surfactant solution over the critical micellar concentration is used. Micelles bound to metal ions and are large enough to be rejected by UF membranes (Mungray et al. 2012).

Cross-References

- [Heavy Metal Recovery by Membrane Operations](#)
- [Heavy Metal Recovery by Chelating Agents and Membranes](#)
- [Nanofiltration](#)
- [Ultrafiltration \(UF\)](#)

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Hemodialysis (HD) Membranes

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Introduction

Hemodialysis (HD) consists in recirculating the patient's blood into a hemodialyzer with an ultrafiltration membrane which permits to remove uremic toxins mainly by diffusion, while excess

water is removed by ultrafiltration. The treatment of chronic renal disease requires three dialysis sessions of 4 h per week, as well as dietetic restrictions to limit potassium intake. In 2008, 1.58 millions of patients were treated by HD worldwide. Without reuse, assuming a mean membrane area of 0.9 m^2 per hemodialyzer, they would have consumed $213 \cdot 10^6 \text{ m}^2$ of membrane per year. If 75 % of dialysis centers reuse dialyzers 2.54 times (Chuang et al. 2008), this consumption is reduced to $116 \cdot 10^6 \text{ m}^2$, which is still the biggest application of membranes. The first disposable hemodialyzers were commercialized in 1950, but it is the arteriovenous shunt invented by Dr. Scriber from Seattle which permitted modern dialysis by connecting the dialyzer inlet to an arm artery and the outlet with an arm vein, permitting a blood flow rate of 200–300 ml/min into the dialyzer.

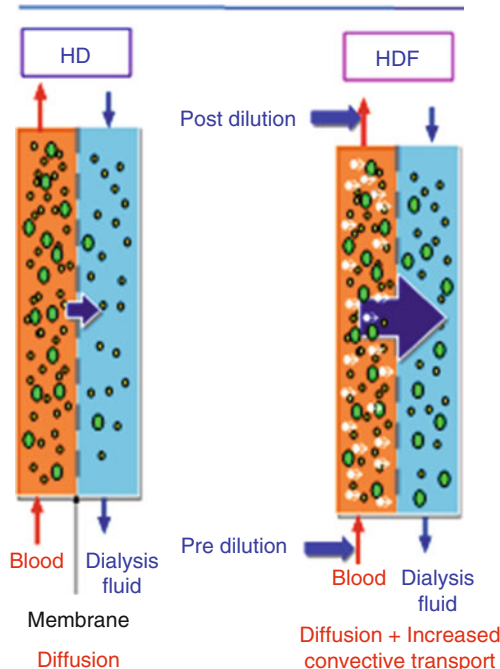
Physiological Requirements

Dialysis must reproduce the four main functions of kidney:

- Elimination of uremic toxins, urea, creatinine, uric acid, phosphates, and sulfates
- Removal of excess body water by ultrafiltration, 1–3 L per run
- Control of plasma electrolytes concentrations Na^+ , Cl^- , K^+ , Ca^{++} , by adjusting dialysate ionic concentration
- Maintaining blood pH to 7.2 through an acetate or bicarbonate buffer in dialysate

In regular hemodialysis, only the excess water is removed by ultrafiltration, while in hemodiafiltration (HDF) about 10–20 L of water is removed from blood per session to eliminate toxins and middle molecules by convection in addition to diffusion, and it is replaced by a sterile dialysate except for the part corresponding to excess water. Figure 1 illustrates the difference between HD and HDF. In predilution mode, the sterile dialysate is reinjected in blood at dialyzer inlet, while it is reinjected at outlet in postdilution. Hemofiltration (HF) is analogous to HDF with up to 25 L water removal, but without feeding dialysate in the dialyzer as toxin removal by diffusion is not necessary.

Hemodialysis (HD) and Hemodiafiltration (HDF)



Hemodialysis (HD) Membranes, Fig. 1 Difference between HD and HF modes

Dialysis Membranes

They are divided into two categories, low and middle permeability cellulosic membranes and high permeability polymeric membranes, which are listed in Table 1. They are generally of hollow fiber geometry (200 μm diameter), but some flat sheet membranes are also available. Cuprophane membranes are now replaced by cellulose acetate or triacetate which is more biocompatible, even though they activate complement and leukocytes, leading to inflammatory reaction (Bouré and Vanholder 2004). Masking hydroxyl groups increases their biocompatibility. High permeability membranes permit to carry out hemodiafiltration and hemofiltration treatments with high water removal, partially replaced by sterile dialysate. In addition, polymeric membranes are often more biocompatible than cellulosic ones. They are also superior for patient quality of life, reducing $\beta_2\text{-M}$ amyloidosis, infections, and loss of residual kidney function.

Hemodialysis (HD) Membranes, Table 1 Hemodialysis membranes

Type	Plane	Fiber	Manufacturer		Permeability ml/h-mmHg m ²
			Membrane	Dialyzer	
Low and middle permeability,					
Cuprophane	X	X	AKZO	Baxter, Bellco, Gambro	2–3.5
Cuprophane HDF	X		AKZO	Gambro	8
Cuprophane TAF		X	Terumo	Terumo	
Hemophane	X		AKZO	CD Medical	
Cellulose acetate	X				5
Cellulose triacetate	X			Baxter, Nipro	
High permeability					
PMMA		X	Toray	Toray	14
Polyacrylonitrile PAN	X	X	Hospal	Hospal, Asahi	25
PAN S		X	Hospal	Hospal	40
Polysulfone		X	Fresenius	Fresenius	30–40
Polysulfone		X	Amicon (HF)	Amicon	50
Polyamide		X	Gambro (HF)	Gambro	30

High-flux membranes with larger pores increase removal of middle molecules such as β_2 -microglobulin, cytokines, resistin, immunoglobulins, parathyroid hormones, and dinucleoside polyphosphates. Their removal protects the patient against cardiovascular problems and other side effects of uremic syndrome (Vanholder et al. 2011).

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Characteristics of Recent European Hemodialyzers

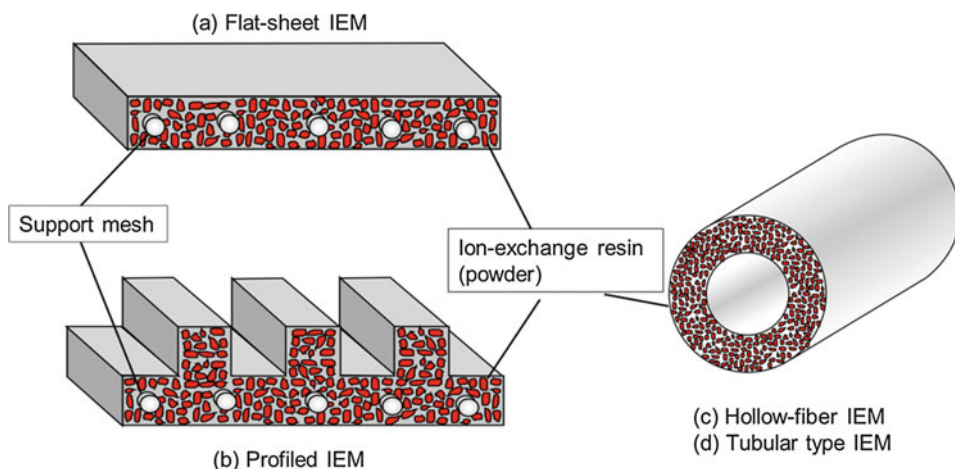
Hospal Gambro (Meyzieu, France) commercializes three high-flux hollow fibers dialyzers: the Evodial with heparin grafted to AN membrane, giving very good hemocompatibility; the Nephral ST with PEI, a biopolymer grafted on AN69; and the Revaclear with a Poractron membrane permitting to reduce its area. Gambro (Sweden) sells, for HF and HDF, the polyflux H with a polyamide–polyacrylether sulfone membrane. Fresenius Medical Care (Germany) commercializes high-flux dialyzers with a Helixone membrane, the FX60, 800, and 1,000 with urea clearances of up to 278 ml/min at a blood flow of 300 ml/min, and other dialyzers with polysulfone membrane, both at high flux (F 40S to F80S with area from 1 to 1.8 m²) and at low flux (F4HPS to F8HPS with area from 0.7 to 2.4 m² according to patient weight).

Heterogeneous Ion-Exchange Membranes

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Heterogeneous ion-exchange membrane consists of finely powdered ion exchanger and a binder polymer, and, in many cases, the membrane is reinforced by woven cloth or net to improve its mechanical properties. In general, heterogeneous ion-exchange membranes (IEMs) are prepared by the following method (Sata 2004): finely powdered organic and/or inorganic ion exchanger is homogeneously mixed and heated with a thermoplastic polymer such as poly(vinyl chloride),



Heterogeneous Ion-Exchange Membranes, Fig. 1 Schematic diagram of heterogeneous IEMs with various kinds of shapes



Heterogeneous Ion-Exchange Membranes, Fig. 2 Tubular-type heterogeneous IEM, EDCORE

polyethylene, polypropylene, or other engineering plastics, and then the mixture is formed into the membrane by pressing and/or heating. Heterogeneous IEMs have slightly lower electrochemical properties: lower permselectivity for counterions and/or higher membrane resistance than homogeneous ion-exchange membrane. However, heterogeneous IEMs are easily prepared and have high mechanical strength. Moreover, the IEMs of various kinds of shapes can be easily prepared by pressing and/or heating as shown in Fig. 1: (a) commercial flat-sheet IEMs such as Ralex CMH and AMH (Mega a.s., Czech Republic), (b) profiled IEM for reverse electrolyte applications (Vermaas et al. 2011), (c) hollow fiber-type IEMs (Kiyono et al. 2004), and (d) commercial tubular-type IEMs (EDCORE,

Astom. Co., Ltd., Japan). EDCORE is a membrane electrode apparatus, with smooth-surfaced seamless and tubular IEMs (Fig. 2), and is used in industries such as electro-deposition painting of automobile, building materials, house appliance, and other applications due to their high mechanical strength and ease of handling.

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Heterogenization or Immobilization of a Catalyst

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The heterogenization or immobilization of a catalyst in/on a membrane consists in the

incorporation of a catalyst in/on a membrane by chemical bonds or physical entrapment.

In the case of a homogeneous catalyst, the incorporation constitutes a way to heterogenize it.

When a catalyst is incorporated within or on the surface of a membrane, the membrane composition (characteristics of the membrane material, hydrophobic or hydrophilic, presence of chemical groups with specific functionality, etc.) and the membrane structure (dense or porous, symmetric or asymmetric) can positively influence the catalyst performance, not only by the selective absorption and transport of reagents and/or products but also influencing the catalyst activity by electronic and conformational effect.

The main requirements that must be considered to produce an “ideal catalyst” are: low costs, high selectivity, high stability under reaction conditions, nontoxicity, “green properties,” and first of all recoverability, i.e., the possibility to recover and reuse the catalyst (Gładysz 2001; Hill 1999).

In this perspective, the heterogenization of catalysts has interesting implications because it allows the reuse several times of the same catalyst. Among the different heterogenization methods, the entrapping of a catalyst in/on a membrane offers new possibility for the design of new catalytic processes.

In addition to the fundamental criteria that have to be considered in the selection of a membrane for a specific separation process, i.e.:

- Stability (mechanical, thermal, and chemical)
- Permeability and selectivity
- Fouling tendency
- Cost (capital and operating)

Extra technical complexities need to be considered in the design and realization of catalytic membranes:

- Catalyst stability during the immobilization procedure
- Influence of the catalyst particles on the membrane properties (mechanical, transport, etc.)
- Effect of the catalyst loading, dimensions, and distribution, on the catalytic efficiency

- Leaching out from the membrane of the catalyst

However, catalytic membranes deserve special advantages that in many cases justify these additional efforts.

In the design of a catalytic membrane, major issues in the polymer selection are the mechanical, thermal, and chemical stability under reaction conditions.

What is fundamental is to realize a stable catalyst immobilization in order to avoid its leaching out from the membrane. Different immobilization strategies can be used in order to achieve these goals: covalent bonds, electrostatic and weak interactions (van der Waals or hydrogen bonds) of the catalyst with the membrane, or catalyst encapsulation.

A good affinity for the catalyst is desirable in order to avoid catalyst leaching and to have a good adhesion between the polymer and the catalyst, with an optimal dispersion of the second one.

The affinity between a compound and a polymeric material can be often anticipated by the calculation of the *affinity parameters* (Van Krevelen 1990; Barton 1990). These parameters reflect the ability to form hydrogen bond, polar, and van der Waals interactions in condensed phase.

The polymer/catalyst affinity can be also improved by an appropriate chemical functionalization of one or both components.

In the case of application in liquid phase, ideally, the solvent used for the reaction needs to be a non-solvent for the catalyst, and the membrane has not to have an excessive swelling in it.

It is also possible in some cases to improve the catalyst retention in the membrane by the catalyst enlargement as: dendrimers, hyperbranched polymers, and catalyst bound to a soluble polymer (Dioos et al. 2006).

Mass transfer of the reagents to the catalytic sites, and of the products away from them, should be fast enough in order to not limit the reaction, but, at the same time, the contact time catalyst/reagent should be also appropriate.

For a porous membrane, the choice of the polymer material is of less importance for

transport properties in comparison with a dense membrane, because permeation does not take place through the polymer matrix, but through the membrane pores (Vankelecom 2002).

However, the membrane material is relevant for the membrane stability and surface properties, such as wettability and fouling tendency.

The membrane preparation conditions depend on the membrane material and the desired structure and morphology. In the case of a catalytic membrane, the incorporation of the catalyst complicates the process because the catalyst should be firmly entrapped in the membrane and the catalyst structure and activity has to be preserved during the membrane preparation procedure.

Moreover, the properties (including transport properties) of the catalytic membrane are usually different than those of the reference membrane prepared in the same conditions but without the catalyst.

Different techniques for membrane preparation are today available and can be opportunely employed also to prepare catalytic membranes: phase separation, coating, interfacial polymerization, sintering, stretching, and track etching are some examples (Strathmann et al. 2006).

In some cases, the catalyst is entrapped in/on the membrane already formed, by covalent bonds, electrostatic interactions, absorption by weak interactions, or physical entrapment. In alternative, the catalyst immobilization can be carried out in the same time of the membrane formation, for example, by dispersing the catalyst in the polymer casting solution and successive phase separation (Drioli and Fontananova 2010).

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Heteropolyacid Composite Membranes

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Heteropolyacid composite membranes are membranes functionalized with heteropolyacids (HPAs).

Acid catalysis and catalytic oxidation are two of the main application areas of HPAs composite membranes. Moreover, interesting examples of HPAs immobilized in membranes are present in the field of the polymer electrolyte membrane fuel cells (PEMFCs) (Norby 1999).

There are many different structural types of HPAs, but the Keggin type (Mioč et al. 2005) is the most common for the majority of the applications as catalysts or solid state proton conductors.

The HPAs discussed in the following text are molybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$), phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$), and silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$).

Catalysis by heteropoly acids has well-established industrial applications including heterogeneous catalyzed selective oxidations (oxidation of methacrolein to methacrylic acid and ethylene to acetic acid) and acid-catalyzed reactions (homogeneous liquid-phase hydration of olefins, biphasic polymerization of THF to

poly(tetramethylene glycol) and the gas-phase synthesis of ethyl acetate from ethylene and acetic) (Kozhevnikov 2007).

Nevertheless, in many processes using HPA catalysts, there are relevant difficulties concerning catalyst separation and recovery and reaction selectivity. In this perspective, the heterogenization of HPAs in membranes can offer important advantages in catalysis by the integration of the catalytic activity with the selective transport through the membranes.

Hydration of α -pinene to α -terpineol over molybdophosphoric acid entrapped in polyvinyl alcohol (PVA) membranes cross-linked with succinic acid, and molybdophosphoric acid encaged in zeolites and dispersed in polydimethylsiloxane (PDMS) membranes, have been reported in literature (Castanheiro et al. 2003). In both cases, the catalytic activity of the membranes is quite good in successive runs although a partial catalyst leaching was observed.

Catalytic membranes have been prepared by linking phosphotungstic acid on the surface of plasma-modified membranes made of polyvinylidene fluoride (PVDF). The PVDF membranes was modified by plasma treatments on the surface, in order to graft N-containing polar groups able to act as binding sites with phosphotungstic acid. The catalytic activity of the membranes has been evaluated in the aerobic degradation reaction of phenol in water (Fontananova et al. 2006). Higher phenol degradation rate was observed for the HPA heterogenized on PVDF membrane compared to homogeneous catalyst dissolved in solution. Moreover, the catalytic membranes have given proof of their complete stability under photooxidation condition and their good recycle.

In numerous literature studies, it has been reported that the HPAs can reduce the resistance to the proton transport in PEMFCs.

The reduction of the HPAs particles sizes and their good dispersion inside the polymeric matrix resulted to be key factors in order to have a positive effect on the proton conductivity because of the increase of the surface to volume ratio of the additives and the possibility to have a more efficient proton hopping (Ramani et al. 2005).

HPAs typically exist in hydrated phase with the degree of hydration varying from 6 to 30 molecules of water, depending on the temperature and the relative humidity (e.g., six molecules of water are present in the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ structure up to 175–230 °C) (Mioč et al. 2005). In Keggin-type HPAs, hydrogen bonds exist between each acid proton and two water molecules, are also present between water molecules and the terminal oxygen atoms of the HPAs, and moreover, involving different Keggin units (Moffat 1986).

If the HPA sizes are in the order of a few nanometers and uniformly distributed in the proton exchange membrane, the water hydration molecules and/or dioxonium ions of the additive can be used to better interconnect the ionic cluster of the polymeric matrix providing a better pathway for proton hopping (Ramani et al. 2005).

Composite membranes with higher glass transition temperature (T_g) and higher stability of the proton conductivity at high temperature have been obtained by incorporation of 60 wt.% of three different HPAs ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{Na}_2\text{HPW}_{12}\text{O}_{40}$) in SPEEK membranes with 70 %, 74 %, and 80 % degree of sulfonation (Zaidi et al. 2000).

Hybrid membranes prepared from sulfonated polyetherketone (SPEK), heteropoly acids, and an inorganic network of ZrO_2 or $\text{RSiO}_{3/2}$ have been also prepared obtaining a higher proton conductivity of the membranes (Ponce et al. 2003).

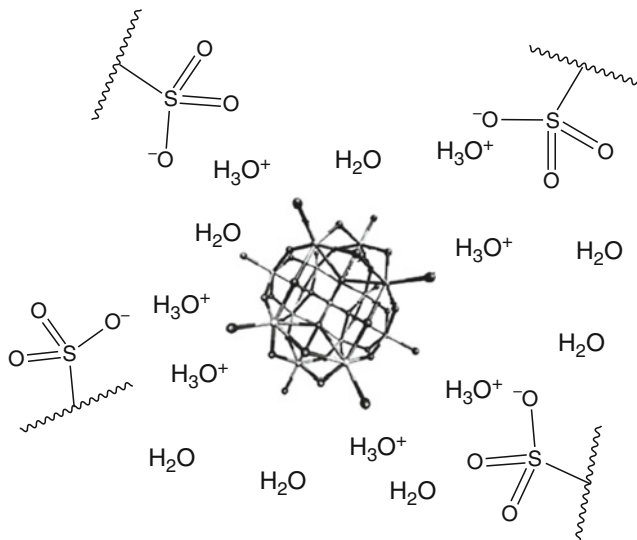
The HPAs have been also used to stabilize the proton conductivity of the Nafion membranes at elevated temperature and low relative humidity. For example, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, also exchanged with larger cations such as Cs^+ , NH_4^+ , Rb^+ , and Ti^+ , has been heterogenized in Nafion membranes observing better proton conductivity (Ramani et al. 2005).

Tungstophosphoric acid, silicotungstic acid, and phosphomolybdic acid have been used as functional additives in composite membranes made of the sulfonated derivative of an amorphous-modified polyetheretherketone, called SPEEK-WC (Fontananova et al. 2010).

The embedding of the inorganic HPAs, in particular the $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, in SPEEK-WC membranes, enhanced the proton conductivity

Heteropolyacid Composite Membranes,

Fig. 1 Schematic view of the interactions by hydrogen bonds between a heteropoly acid (the Keggin structure is represented) with the sulfonic group of a cation exchange membrane, the water hydration molecules, and dioxonium ions



because the HPAs improved the interconnection of the ionic clusters in the polymeric matrix providing a preferential pathway for proton hopping (Fig. 1).

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Heteropolyacids

Ubavka B. Mioč

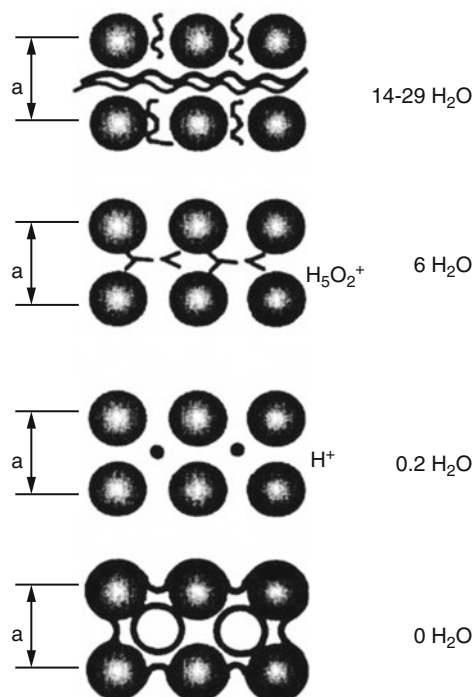
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The basic structural unit in heteropolyacids (HPAs) is the Keggin's cluster (find "Keggin's structure"). Groups are distributed in a three-dimensional lattice and are interconnected by hydrogen-bonded water molecules or some other proton species (OH^- , H_2O , H_3O^+ , H_5O_2^+) forming the secondary structure of Keggin's anion. Water molecules fill channels in solid HPAs, and next interactions, $\text{OH}^- \dots \text{H}_2\text{O}$, $\text{H}_2\text{O} \dots \text{H}_2\text{O}$ and $\text{H}_3\text{O}^+ \dots \text{H}_2\text{O}$, are identified.

Empirical $R_{O...O}$ distances, between 294 and 263 nm, correspond to weak and medium hydrogen bonds.

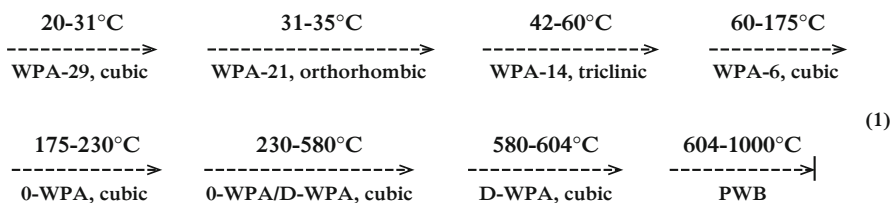
Three best-known acids have been investigated: $H_3PMo_{12}O_{40} \times 29H_2O$ (MoPA), $H_3PW_{12}O_{40} \times 29H_2O$ (WPA), and $H_4SiW_{12}O_{40} \times 30H_2O$ (WSiA). All three acids are isostructural. Among HPAs 12-tungstophosphoric acid hydrates, characterized by strong acidity, are classified into “superacids” (Okuhara et al. 2004). From mother solutions HPAs crystallize with high number of water molecules, 29–30, forming quasi liquid state. Acids are very sensitive to ambient conditions: relative humidity and temperature, and lose very easily water molecules and change to lower hydrates, Eq. 1 and Fig. 1. On the other hand, dehydrated acids are very hygroscopic.

Therefore it is interesting and necessary to see how these compounds change in process of calcination/dehydration and to determine structural phase transition and temperature regions of their stabilities, Fig. 2. Investigations have to be multidisciplinary and different physicochemical methods have to be used. Thermal analysis (TGA, DTA), XRPD, IR, and Raman spectroscopy are recommended for the beginning (Pope and Müller 1994; Mioč et al. 1990, 1994, 2005). Thanks to such investigations besides the phase transition to different crystal hydrates: –29, –21, –14, and –6 hydrates, dehydrated phase, WPA-0, at about 230 °C, was defined as cubic phase. It was postulated that Keggin’s anions of WPA-0 phase are stabilized by protons – “free protons.”



Heteropolyacids, Fig. 1 Schematic survey of different steps of hydration of HPAs

At higher temperatures, about 400 °C (the broad peak) was defined as T_g anomaly on DTA curves. It corresponds to exothermic transformation which is followed by the mass loss (TGA) corresponding to about 0.5–0.3 water molecules.

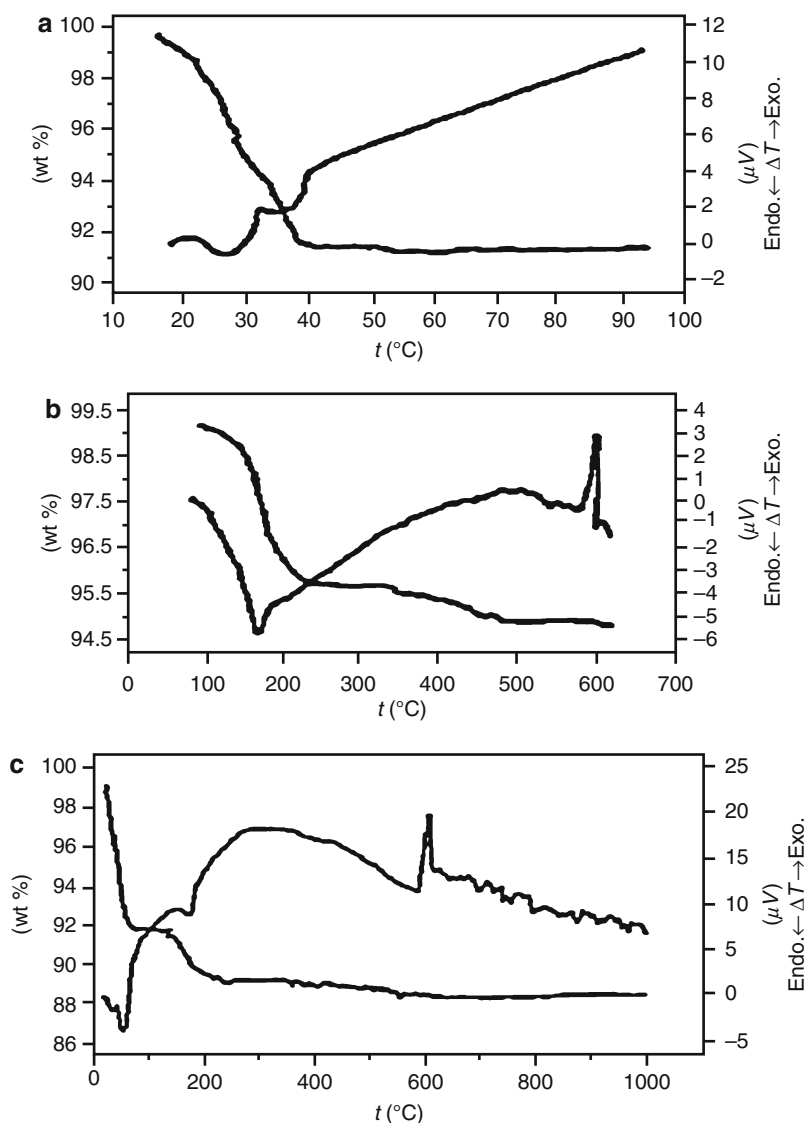


It was evident that these water molecules are formed from protons and few oxygen atoms from host lattice in endothermic process, which is simultaneous with water dehydration.

Nowadays, this water is called protonated (Janik et al. 2004). Metastable (D-phase–denuded phase) is stable up to 604 °C, for WPA, when structural phase transformation to phosphate tungsten

Heteropolyacids,

Fig. 2 DTA and TGA curves of WPA-29 in different temperature regions. Scanning rates were 1, 5, and 10 °C/min



DTA and TGA curves of 29-WPA at temperatures up to 1000 C

bronzes (PWB) happen (Mioč et al. 1994, 2005). All WPA phases were indexed and corresponding unit cell dimension calculated. Some of them for the first time: WPA-14 as triclinic. All phases from WPA-6 up to structural phase transformation are cubic. Phosphate tungsten bronzes (PWB) have also been obtained and defined for the first time using HPAs as precursor (Mioč et al. 1994). Fournier noted also the same large peak for WPA and identified it as a new Q phase.

He claims that a new Q phase is formed after the loss of “constitutional” water (Fournier et al. 1992).

These investigations have been followed by IR and Raman spectroscopic study in situ, in temperature range from temperature of liquid nitrogen -195 to 220 $^{\circ}C$, and with ^{18}O -labeled compounds. On the basis of the obtained spectra, few proton species were identified ($H_5O_2^+$, H_3O^+ , H_2O , and OH^- groups): terminal OH^- groups of

Keggin's anions at about 3,550; OH^- groups from water molecules, due to the most frequent interaction $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ at about 3,490; and OH bands belonging to $\text{H}_3\text{O}^+ \cdots \text{H}_2\text{O}$, the strongest interaction at about 3,292 and 3,225 and 3,140 cm^{-1} ; bands in the region 2,250–2,050 were assigned to ν_3 and/or ν_4 of H_3O^+ and water libration modes. Dioxonium ion was identified also, thanks to the band ν_4 at 1,720 and ν_2 at about 1,220 cm^{-1} . Special attention in the process of calcination/dehydration was paid to the intensity changes of bands $\nu_4(\text{H}_3\text{O}^+)$ at 1,720 and $\nu_2(\text{H}_2\text{O})$ at 1,610 cm^{-1} (Mioč et al. 1990, 1994, 2005).

Protonic entities and their dynamic equilibrium influence the host structure too. Identification of proton species and following of its dynamic equilibrium is also very important for understanding catalytic (formation of Brønsted acid centers) and conductive processes (defining charge carriers, conductivity dependence of temperature, frequency, and so on) as characteristics of these compounds.

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Hexavalent Chromium Separation by Supported Liquid Membranes

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The removal and/or recovery of heavy metals from industrial wastewater is a major topic of research. Chromium is a unique, toxic heavy metal released in aqueous environment in both +3 and +6 oxidation states. Hexavalent chromium (Cr(VI)) receives particular attention because of its mutagenic, teratogenic and carcinogenic properties. Cr(VI) exists as anionic species, such as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and CrO_4^{2-} , which are highly mobile on subsurface environment (Kumbasar 2008). These anionic species are bioaccumulative, and their oxidizing potentials make them highly toxic to biological systems. The major industries that contribute to water pollution by chromium are mining, leather tanning, textile dyeing, electroplating, metal finishing, and corrosion inhibition (Rajasimman and Karthic 2010).

The World Health Organization recommends the toxic limits of Cr(VI) in wastewaters at the level of 0.005 mg/L. Many countries have regulations of the maximum permissible concentration of Cr(VI) in natural or drinking water which typical tolerance limit for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L. Usually Cr(VI) concentrations in industrial wastewaters range from 0.5 to 270,000 mg/L. Then chromium-bearing wastewaters must be discharged into aquatic environments or onto land after appropriate treatments to drastically reduce Cr(VI) content.

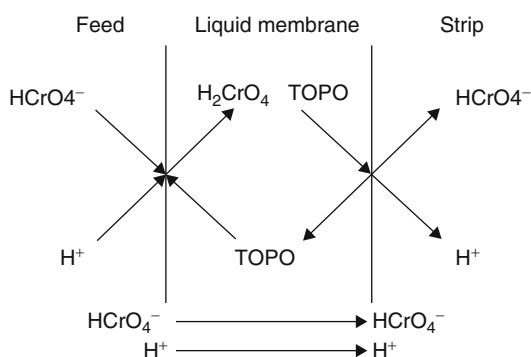
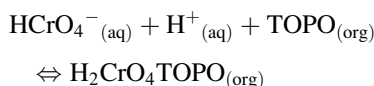
The methodologies for Cr(VI) recovery, from industrial wastewater, range from ion exchange to solvent extraction, non-dispersive solvent extraction, precipitation, and adsorption. Solvent extraction has been widely used for the removal and/or recovery of chromium in hydrometallurgy since this technique allows the Cr ions recovery, but it involves high capital and operating costs due to

large inventory of solvent, especially in the case of dilute solutions. Conventionally the treatment chromium-bearing wastewaters consists of the reduction of Cr(VI) to Cr(III) with an adequate chemical-reducing agent. Cr(III) is then easily precipitated by the addition of an alkali compound (generally calcium hydroxide) to the liquid effluent. The main drawback of this method is the production of a large amount of sludge-containing chromium often in high concentration, which disposal/treatment is a very costly affair and it is not eco-friendly.

Supported liquid membrane (SLM) process offers a technology with a low solvent/extractant consumption since it involves in a single stage the extraction and stripping processes, which are generally performed in two separate steps in conventional solvent extraction. SLM consists of a LM phase, impregnated in the pores of a thin hydrophobic microfiltration membrane, kept there by capillary forces. It combines the typical advantages of liquid membrane with the mechanical resistance of solid membranes. The transport across a SLM is mediated by a mobile extractant (carrier) which binds very selectively the target component in the donor phase (feed), transporting it into the acceptor phase (strip), resulting in the so-called facilitated transport (Molinari et al. 2009a, b). The selection of an appropriate carrier provides higher selectivity and enrichment factor as compared to the other separation methodologies.

Despite of their advantages with respect to the traditional separation techniques, SLM is not widely applied in treatment of chromium-bearing wastewaters. Cr(VI) compounds could be removed from dilute aqueous solutions by using trioctylphosphine oxide (TOPO), Alamine 336, tri-n-octylamine (TOA), and tributyl phosphine (TBP) as ionic carrier.

The extraction of HCrO_4^- with TOPO from acidic solutions could be expressed by the following equation (Kumbasar 2009; Hasan et al. 2009):



Hexavalent Chromium Separation by Supported Liquid Membranes, Fig. 1 Schematics of separation mechanism through liquid membrane

The so-formed complex diffuses through the membrane toward the stripping basic solution where the de-complexation reaction takes place and HCrO_4^- and H^+ ions are released. The so-regenerated carrier molecule diffuses back to the feed and the transport cycle begins again (Fig. 1). This transport mechanism is the so-called facilitated coupled co-transport, typical when a basic carrier like amines or phosphates is used to transport negatively charged species (in this case HCrO_4^-) and usually H^+ as counterion across the membrane in the same direction (Fig. 1).

Cr(VI) complexes can be efficiently removed from acidic chloride aqueous solutions by facilitated transport with TOA into a basic (NaOH 0.1 M) acceptor phase (Kozłowski and Walkowiak 2002). In agreement with the transport mechanism that is similar to that one previously reported for TOPO, the permeability coefficient and then initial flux values decrease linearly by increasing the feed pH. Cr(VI) concentration can be successfully reduced in the feed phase from 1.0 to 0.0028 mg/L, thus respecting the World Health Organization's recommendations.

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High Free Volume Polymer

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Free volume is the unoccupied space between molecules. The concept of free volume is used to explain molecular motion in liquids and solids. In a liquid or rubber, free volume increases with increasing temperature. A flexible polymer will flow or behave as a rubber at temperatures at which there is sufficient free volume for large-scale movements of polymer segments but will behave as a glass when the temperature is reduced to the point where there is not enough free volume for such movements.

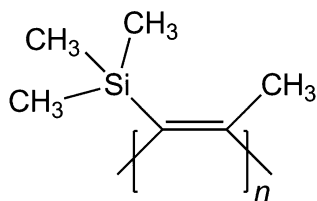
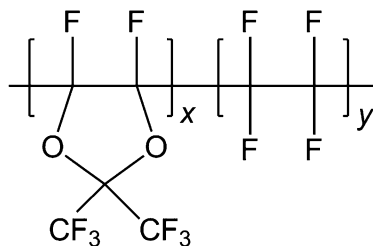
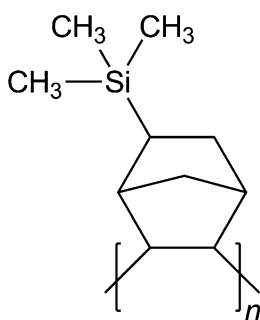
Different assumptions may be made about what constitutes “occupied” and what constitutes “free” volume in a material. Thus, in different contexts, different values may be quoted for the amount of free volume in a polymer. In membrane science, it is common to define fractional free volume as

$$f_v = \frac{V - 1.3V_w}{V}$$

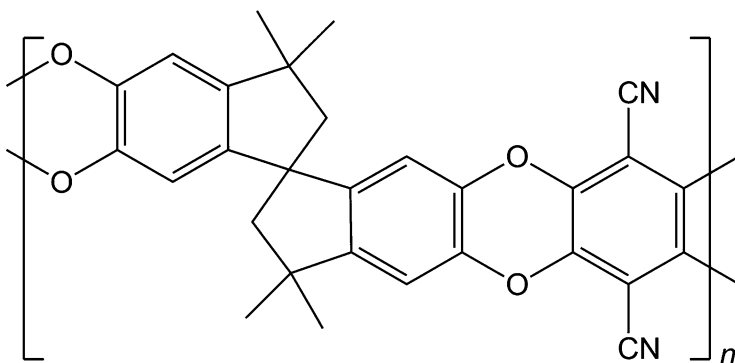
where V is the specific volume (reciprocal of density) and V_w is the specific van der Waals volume, which for many polymers may be estimated using group contribution methods. The factor 1.3 takes account of the fact that molecules cannot completely fill space even in a perfectly ordered crystal at absolute zero and is an average value for crystalline materials. By this definition, most glassy polymers have $f_v < 0.2$. Some glassy polymers, however, have much higher fractional free volumes and consequently exhibit high permeabilities to gases and vapors (Budd and McKeown 2010; Yampolskii 2012; Pinnau and Toy 1996; Starannikova et al. 2008; Thomas et al. 2009). The structures of some polymers with exceptionally high free volume are shown in Fig. 1.

A common feature of high free volume polymers is that they have relatively inflexible, twisted backbones, which cannot change conformation in order to fill space efficiently. In substituted polyacetylenes such as PTMSP, the bulky side group inhibits rotation about single bonds in the backbone and forces the backbone into a twisted shape. In perfluoropolymers such as Teflon AF2400, neighboring dioxolane rings cannot easily rotate past each other. In substituted polynorbornenes prepared by addition polymerization, such as PTMSN, ring structures and bulky side groups restrict rotation about backbone bonds. The ultimate extension of this idea is found in polymers of intrinsic microporosity, such as PIM-1, which have no single bonds in the backbone about which rotation can occur but which incorporate sites of contortion (the spiro centers in PIM-1) to force the backbone to twist and turn.

The polymers shown in Fig. 1 are soluble and can readily be processed from solution to form membranes. However, there are other high free volume polymers which cannot be prepared in soluble form. Sometimes, it is possible to form a membrane from a soluble precursor and subsequently convert it to the desired structure through chemical or thermal treatment. For example,

**PTMSP**
 $f_V = 0.33$ (Hofmann et al. 2002)
**Teflon AF2400** ($x=0.87$, $y=0.13$)
 $f_V = 0.33$ (Pinnau and Toy 1996)
**PTMSN**
 $f_V = 0.28$

(Starannikova et al. 2008)

**PIM-1**
 $f_V = 0.24$ – 0.26 (Thomas et al. 2009)

High Free Volume Polymer, Fig. 1 Molecular structures and fractional free volumes of poly(1-trimethylsilyl-1-propyne) (PTMSP), a copolymer of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and tetrafluoroethylene (Teflon AF2400), addition-type poly(trimethylsilyl norbornene)

(PTMSN), and a polymer of intrinsic microporosity prepared from 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane and 1,4-dicyanotetrafluorobenzene (PIM-1)

polybenzoxazole structures can be prepared by thermal rearrangement from aromatic hydroxyl-containing polyimides (Park et al. 2007).

The permeation of gases and vapors through a polymer depends not only on the amount of free volume but also on the size, distribution, and connectivity of free volume elements. Computer simulation is useful for visualizing the free volume distribution in amorphous polymers (Hofmann et al. 2002). A number of experimental techniques, notably positron annihilation lifetime spectroscopy (PALS), have been employed to obtain information about the size and distribution of free volume elements. In a high free volume polymer, there may be sufficient connectivity between free volume elements for the polymer to behave like a molecular sieve or microporous

material (pore size <2 nm) (Rutherford 2001), in which case the apparent micropore distribution can be determined from gas adsorption studies (McKeown and Budd 2010).

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High Selective Carbon Membranes

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In general, carbon membranes prepared under appropriate conditions show higher selectivities in gas separations than do conventional polymer membranes (Ismail and David 2001; Saufi and Ismail 2004; Kita 2006; Ismail and Li 2008; Williams and Koros 2008; Yoshimune and Haraya 2011). Examples of O_2/N_2 separation performances of carbon membranes, taken from literature sources, are plotted in Fig. 1, which also shows the upper limits for polymer membranes (Kita et al. 1997; Suda and Haraya 1997; Shiflett and Foley 2000; Ghosal and Koros 2000; Kim et al. 2004, 2005; Shao et al. 2004; Yoshimune et al. 2005; Xiao et al. 2005a, b; Robeson 2008). The carbon membranes were prepared from various precursors, including various aromatic polyimides (Kapton, Matrimid, etc.), polyfurfuryl

alcohol (PFA), a polypyrrolone, and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Results for O_2/N_2 selectivity and O_2 permeability are sometimes used as benchmarks for characterizing the properties of membranes as a function of synthesis variables. It can be clearly seen that most carbon membranes have O_2/N_2 selectivities that are roughly three times higher than the upper limit for polymer membranes when the selectivities are compared at the same O_2 permeability. Previous reports have shown that carbon membranes have considerable promise for commercial applications, not only in O_2/N_2 separation but also in hydrogen purification and the separation of CO_2/CH_4 , CO_2/N_2 , or propene/propane mixtures, which are all processes in which conventional polymer membranes do not perform adequately.

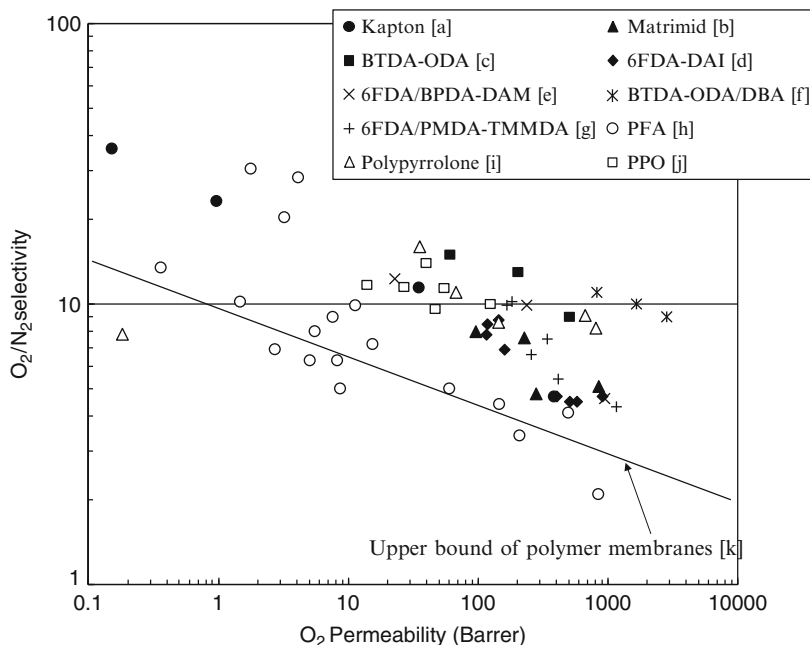
Optimal conditions for the production of carbon membranes vary according to the nature of the precursor polymers and their morphologies, because the various polymers show different thermal decomposition behaviors. Control of the conditions for pyrolysis of the precursor polymer, as discussed below, is the most important factor in increasing the gas selectivity of the resulting carbon membrane, because the nature of the pyrolysis process has a considerable effect on the pore structures of the membrane.

Pyrolysis Temperature

The pyrolysis temperature is generally chosen to be above the decomposition temperature of the polymer, but below its graphitization temperature (500–1000 °C). As a general rule, an increase in the pyrolysis temperature reduces the permeability of the resulting carbon membrane but increases its selectivity. High pyrolysis temperatures produce increased crystallinity and lower average interplanar spacings in carbon membranes, resulting in smaller micropores and sharper pore-size distributions. This behavior certainly depends on the physical properties of the polymer, so that a suitable carbonization temperature needs to be chosen individually for a particular polymer precursor to achieve optimal performance in gas separations.

High Selective Carbon Membranes,

Fig. 1 Comparison of the oxygen permeabilities and selectivities of various carbon membranes with the upper limit for polymer membranes ([a] Suda and Haraya 1997, [b] Xiao et al. 2005a, [c] Kim et al. 2005, [d] Xiao et al. 2005b, [e] Ghosal and Koros 2000, [f] Kim et al. 2004, [g] Shao et al. 2004, [h] Shiftlett and Foley 2000, [i] Kita et al. 1997, [j] Yoshimune et al. 2005, [k] Robeson 2008)



Thermal Soak Time

The thermal soak time can have varied effects on the performance of the final membrane. Changing the thermal soak time, particularly at the final pyrolysis temperature, can be used effectively to fine-tune the permeation properties of a carbon membrane. A prolonged thermal soak time increases the selectivity of carbon membranes but decreases their permeability.

Heating Rate

The heating rate determines the rate of evolution of volatile components from a polymeric membrane during pyrolysis and, consequently, affects the nature of the pores that are formed in the resulting carbon membrane. Lower heating rates (5 °C/min or less) favor the formation of small pores and increase the crystallinity of the resulting carbon, thereby producing carbon membranes with increased selectivities. From the practical

standpoint, however, an optimal heating rate that is not too low should be chosen, because low heating rates increase the costs and time involved in producing carbon membranes.

Another method for tuning the gas selectivities of carbon membranes is the production of mixed-matrix membranes (Yoshimune and Haraya 2011). Mixed-matrix carbon membranes are defined as products of the pyrolysis of membranes consisting of a continuous polymer matrix containing nano-sized inorganic particles dispersed throughout the polymer. Metal ions or particles, silica particles, zeolites, or carbons are normally used as inorganic particles to improve the properties of the resulting membranes. Such nano-sized particles increase the polarity of the membranes, form interlayer spaces, or have an affinity toward target gases.

Figure 2 shows the hydrogen permeability and selectivity of several types of mixed-matrix carbon membranes (Park et al. 2004; Yoda et al. 2004; Park and Lee 2005; Liu et al. 2006; Yoshimune et al. 2006; Grainger and Hägg 2007). Some of the mixed-matrix carbon membranes

High Selective Carbon Membranes,

Fig. 2 Comparison of the hydrogen permeabilities and selectivities of various mixed-matrix carbon membranes with the upper limits for polymer membranes ([a] Suda and Haraya 1997, [k] Robeson 2008, [l] Grainger and Hägg 2007, [m] Yoda et al. 2004, [n] Yoshimune et al. 2006, [o] Park et al. 2004, [p] Park and Lee 2005, [q] Liu et al. 2006)

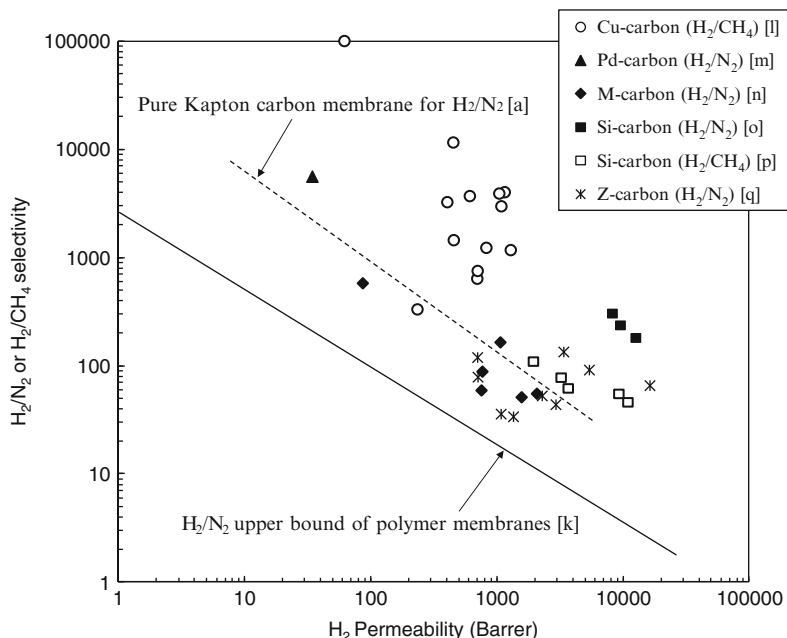


exhibit significantly superior performances in comparison to that of the Kapton-derived carbon membrane, which is shown here as the boundary for pure-carbon membranes. This technique can help to improve the trade-off between the permeability and the selectivity of carbon membranes, as well as provide novel functionalities in membrane reactors.

High selectivity by carbon membranes is generally observed in the case of dense membranes in forms such as flat sheets or hollow fibers. For commercial applications, it is necessary to fabricate membranes into modules that have both a high selectivity and a high permeability. Thinner separation layers, such as asymmetric hollow fibers, in combination with adequate mechanical strength are desirable; however, carbon membranes are brittle in handling, and even a small number of pinholes can ruin their gas selectivity. This hinders the production of carbon membranes on an industrial scale. Although carbon membranes have considerable potential for use, not only in gas and vapor separations but also as membrane reactors, further investigations are needed before they can be used commercially.

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High-Defined Porous Films

► Honeycomb Membrane Structure

Higher (C3+) Hydrocarbon Removal

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Rubbery polymer membrane materials have the ability to permeate preferentially condensable vapors. Rubbery membranes were found to be very profitable for the recovery of high-value monomer in petrochemical plants' purge gases (Table 1). In the case of large polymerization facilities, the value of purge monomers can reach amounts up to two million USD/year.

Higher (C3+) Hydrocarbon Removal, Table 1 Membrane-based olefin recovery from polymer resin degassing vent (MTR Inc. membrane modules) Baker and Jacobs 1996; Baker et al. 2000

Application	Feed composition	Olefin flow rate recovered (recovery yield)
LLDPE/HDPE reactor purge	Butene 36 % Ethylene 41 % Ethane 1 % Nitrogen 21 % Hydrogen 1 %	C2 = 145 kg/h (88 %) nC4 = 142 kg/h (98 %)
HDPE resin degassing	1-butene 57 % CO ₂ /O ₂ 2 % Nitrogen 40 % Water 1 %	iC4 = 1160 kg/h (97 %)
Polypropylene resin degassing	Propylene 14 % Propane 0.3 % Nitrogen 84.4 % Hydrogen 1 % Water 0.3 %	C3 = 500 kg/h (91 %)

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Highly Permeable Polyimides

Mariolino Carta

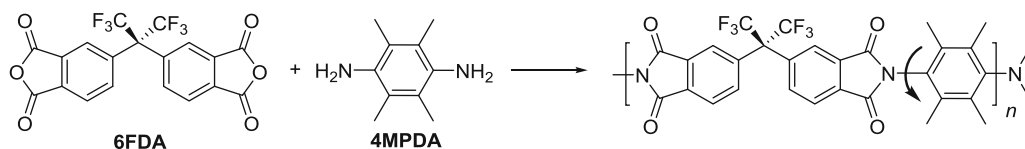
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Polyimides are polymers produced by cycloimidization (formation of an imide linkage) between di-anhydrides and diamines via step-growth polymerization (Koros and Fleming 1993; Ghosh and Mittal 1996). Among other useful applications such as materials for electronics, coatings, foam, and fibers, because of their excellent solubility in common low boiling point solvents, thermal stability, and physical properties, they have been extensively studied as gas separation membranes. A typical limitation for their use in this field is due to the fact that they often exhibit high selectivity but low permeability for important gas pairs such as O₂ and CO₂, usually far below 100 Barrer (1 Barrer = 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹). The low permeability is strongly related with the lack of fractional free volume of the material (FFV) because of the free rotation around the imide linkage that allows the polymer to pack densely, limiting the mass transport. Initial successes in enhancing the permeability by increasing the FFV have been achieved with the use of 4, 4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), which is now one of the

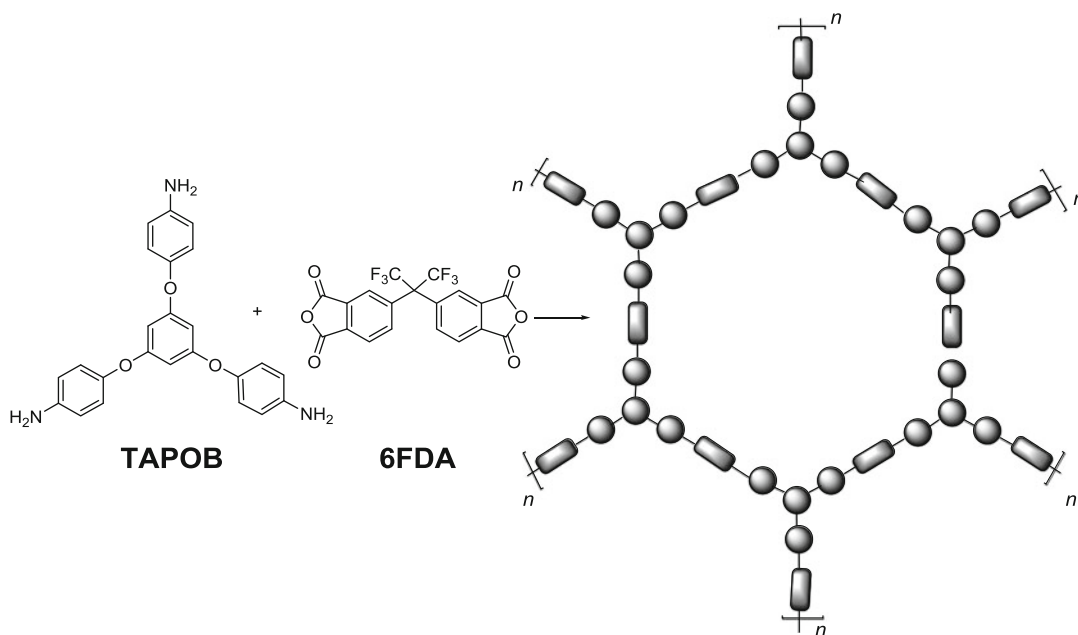
most common monomers for the formation of high-performance polyimides (Fig. 1), and 2,3,5,6-tetramethyl-1, 4-phenylenediamine (4MPDA). The hindrance of the four methyl groups of the di-aniline restricts the rotation around the imide linkage allowing the synthesis of more porous (so less dense) polyimides. The higher porosity facilitates the mass transport of the gases through the pores of the membrane with consequent increase of the permeability (molecular sieving effect), typically over 100 Barrer for O₂ and 400 Barrer for CO₂ with selectivity $\alpha_{\text{O}_2/\text{N}_2} = 3.5$ and $\alpha_{\text{H}_2/\text{N}_2} = 16.6$ (Lin et al. 2000).

A different method to increase the FFV is represented by the formation of hyperbranched polyimides. In this case a triamine monomer, such as 1,3,5-tris(4-aminophenoxy)benzene (TAPOB), is reacted with different di-anhydrides to obtain a highly branched structure (Tsai et al. 2003) (Fig. 2). The polyimides obtained with this technique are insoluble so, to be used as membrane for gas separation, they must be embedded in a support. Typically, it can be prepared by the dispersion of the polyimide with colloidal silica by sol-gel processes, to form a composite material. The most remarkable characteristic of this hyperbranched polymer is that they can be made out of a large variety of A₃ + B₂ terminal groups so that the synthesis can afford different multifunctional polymers.

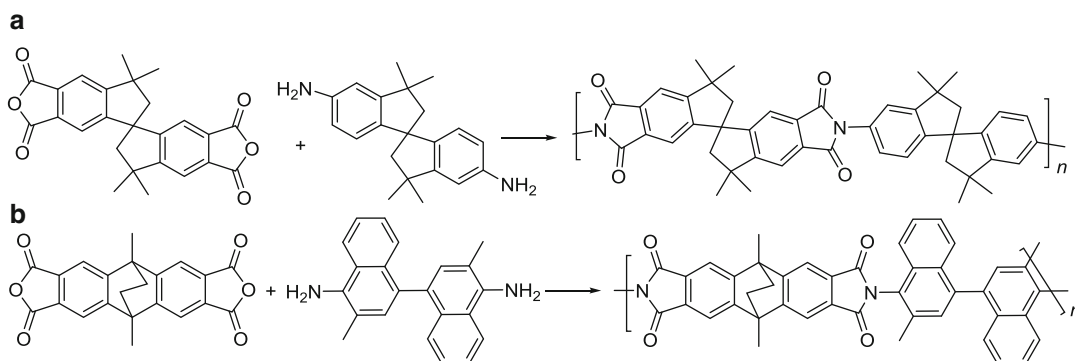
Following the idea of restricting the rotation around the imide link, the concept of *polymers of intrinsic microporosity* (PIMs), which is based on the polymerization of monomers that possess a *site of contortion*, was applied to the synthesis of polyimides. In this case, di-anhydrides and/or di-anilines such as the spirobisindane **A** or the ethanoanthracene **B** (as shown in Fig. 3) are employed. The *site of contortion* is represented



Highly Permeable Polyimides, Fig. 1 6FDA + 4MPDA-based polyimide (Lin et al. 2000)



Highly Permeable Polyimides, Fig. 2 Hyperbranched polyimides (Tsai et al. 2003)



Highly Permeable Polyimides, Fig. 3 Highly permeable polyimides of intrinsic microporosity (Rogan et al. 2014)

by the central quaternary carbon in case of **A** or the methylene bridge for **B** (Rogan et al. 2014). Although there is still free rotation around the imide linkage, the big hindrance of the bulky substituent, combined with the reduced flexibility given by the *site of contortion*, allows the formation of high FFV polymers that cannot pack space efficiently in the solid state, leaving interconnected pores of nano-/microdimension

(for this reason they are called *polymers of intrinsic microporosity*).

Studies on this class of polymers demonstrate that the systematic increase of the rigidity of the structural backbone favors the molecular sieving effect of the material, enhancing both permeability and selectivity for various gas pairs. The resulting PIM-polyimides (PIM-PIs) possess high molecular mass and elevated microporosity,

with BET surface areas in the range of 600–700 m²g^{−1}. These features, associated with the high solubility in common organic solvents, allow the preparation of robust thin-film membranes with excellent performance toward important commercial gas pairs, such as O₂/N₂, H₂/N₂, and CO₂/CH₄, with exceptional permeabilities (over 1000 Barrer for O₂ and over 7000 Barrer for CO₂) accompanied by good selectivities $\alpha_{\text{O}_2/\text{N}_2} = 3.5$, $\alpha_{\text{H}_2/\text{N}_2} = 11.5$, and $\alpha_{\text{CO}_2/\text{CH}_4} = 16.1$. Remarkably, all data points lie above the Robeson upper bounds. With the appropriate choice of the monomers of both di-anhydrides and di-anilines, it is possible to tune the physical properties of these highly permeable polyimides to improve them even further.

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High-Pressure Electrolysis

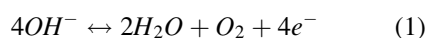
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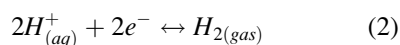
High-pressure electrolysis (also called high-pressure electrolysis HPE) is the water electrolysis performed at pressures higher than ambient in which electrical energy is the driving force of the water decomposition to produce oxygen (O₂) and hydrogen (H₂). The core of an electrolysis unit is an electrochemical cell, which is filled with pure

water and has two electrodes connected with an external power supply. Electric current causes positively charged hydrogen ions to migrate to the negatively charged cathode, where a reduction takes place in order to form hydrogen atoms. The atoms formed then combine to form gaseous hydrogen molecules (Eq. 1). On the other hand, oxygen is formed at the other electrode (the positively charged anode) (Eq. 2). The amount of gases produced per unit time is directly related to the current that passes through the electrochemical cell (Wendt and Kreysa 1999).

Oxygen and hydrogen gas can be generated at noble metal electrodes by the electrolysis of water: Positive electrode (anode):



Negative electrode (cathode):



In a differential pressure configuration, only the cathode (hydrogen) side is under pressure, and this can eliminate the hazards related to handling pressurized oxygen. The high-pressure operation of an electrolyser brings the advantage of delivering hydrogen at a high pressure (sometimes called electrochemical compression) for the end user, thus requiring less energy to further compress and store the hydrogen. It also diminishes the volume of the gaseous phase at the electrodes thus significantly improving product gas removal which follows Fick's law of diffusion (Carmo et al. 2013).

A number of advantages can be gained from operating an electrolyser at high pressure; on the one hand, specific power consumption is reduced, then the cost of gas compressors is reduced or eliminated by delivery of gas pressure, and finally, the size of electrolysis cells is reduced. Though the reversible cell voltage increases theoretically with pressure, the overvoltage is reduced by higher operating pressure and decreased gas volume, and a small overall reduction in the cell voltage is usually found (Zoulias et al. 2004).

Types of Electrolysers

The electrolyser unit consists in the simplest principle of two electrodes separated by an electrolyte. The role of the electrolyte is to close the electrical circuit by allowing ions (but not electrons) to move between the electrodes. Moreover it keeps the produced gases separated. Three common types of electrolysers are used: (i) alkaline electrolysers, (ii) polymer electrolyte membrane (PEM) electrolysers, and (iii) solid oxide electrolysis cells (SOECs).

Alkaline electrolysers (AEC) represent a very mature technology that is the current standard for large-scale electrolysis. The anode and cathode materials in these systems are typically made of nickel-plated steel and steel, respectively. The electrolyte in these systems is a liquid based on a highly caustic KOH solution. The ionic charge carrier is the hydroxyl ion, OH⁻, and a membrane porous to hydroxyl ions, but not to H₂, and O₂ provides gas separation. Key advantages of this technology include its maturity and its durability. Key disadvantages are its use of a highly caustic electrolyte and its inability to produce hydrogen at high pressures (Jensen et al. 2008). This inability to produce high-pressure hydrogen for storage results in the added need for an external compressor, which adds cost and complexity to the system.

Water electrolysis by solid oxide electrolysis cells (SOECs) is principally performed at temperatures in between 700 °C and 1000 °C (see entry ► [High-Temperature Electrolysis](#)) due to the H₂ electrolysis reaction which becomes increasingly endothermic with temperature and the ohmic losses in SOECs which decrease with increasing temperature. The high temperature allows hydrogen production with significantly reduced electrical energy demand (Larminie and Dicks 2003).

In an acidic polymer electrolyte membrane (PEM) electrolysis cell, water splitting is performed according to the reactions shown by (Eqs. 1 and 2). Protons are formed at the anode under water consumption, where the oxygen evolution reaction (OER) takes place. The protons migrate through the solid polymer electrolyte (SPE) membrane to the cathode, where they are reduced into hydrogen. The polymer electrolyte

membrane (Nafion[®], fumapem[®]) provides high proton conductivity, low gas crossover, compact system design, and high-pressure operation (Carmo et al. 2013).

The reinforcement of the cells with metallic support on the anode side allows the generation of hydrogen at high pressures (up to 160 bar commercial units) (Badwal et al. 2013). The energy penalty for generating hydrogen at higher pressures is very small, that is, an order of magnitude increase in hydrogen pressure requires only ~30 mV per cell increase in voltage (as shown by Nernst equation).

PEM electrolysis cells achieve high current densities already at low operational temperatures from 20 °C to 100 °C. PEM electrolysers are not utilized in market applications to the same extent as alkaline ones due to the high investment costs. One of the most important components of such a unit is a separating membrane that allows the passage of ions, or electrons and not oxygen, or hydrogen atoms. This membrane allows the gases to be kept separate in order to avoid the risk of an explosive mixture being formed in the electrolysis unit. The pressure increase minimizes the expansion and dehydration of the membrane, preserving the integrity of the catalytic layer (Grigorev et al. 2001). The membrane technology enables safe differential pressure operation, which in turn allows the electrolysis unit to be operated in a load-following mode with 100 % turndown capability, which is very attractive for renewable energy applications.

The electrolyser utilizes pure water as the circulating fluid, which results in a simpler balance of plant. The differential pressure also results in the ability to operate the oxygen-water fluid loop at ambient pressure, which has significant safety advantages as well as use of plastic tubing rather than expensive high-pressure piping.

The one disadvantage is the acidic environment within the membrane, which limits the catalysts to noble metal oxides and requires semiprecious metals in the oxygen flow fields. The ion exchange membrane is also more sensitive to impurities than the liquid electrolyte, since cations can bind to the proton-conducting sites, reducing conductivity (Zoulias et al. 2004).

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High-Rejection Seawater Reverse Osmosis Membrane

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Introduction

Seawater desalination to convert seawater to potable water by reverse osmosis (RO) membranes has become a pivotal technology to meet the increasing water demand. The RO membrane has a unique property that allows passage of water with little hindrance while presenting a

virtually impermeable barrier to salts and other components. Over the years, it has evolved from the first-generation asymmetric cellulose acetate (CA) membrane to the current generation thin film composite (TFC) membranes with better salt retention and higher water permeability, which has significantly improved the water quality and reduced the energy consumption and costs of seawater desalination.

Structure of TFC RO Membrane and Separation Mechanism

TFC RO membrane, prepared using interfacial polymerization technique, is composed of an active skin layer (thickness ~200 nm and pore size of <0.1 nm) commonly made from cross-linked aromatic polyamides, a polysulfone porous support layer (thickness ~50 µm), and a polyester nonwoven fabric substrate (thickness ~100 µm), as shown in Fig. 1 (Kurihara and Tomioka 2010; Uemura et al. 2012).

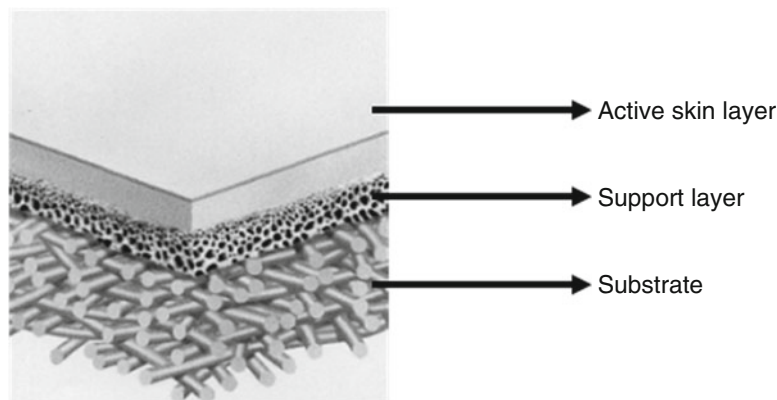
The active layer determines the separation properties, whereas both the support layer and substrate merely provide mechanical support for the active layer to withstand high-operating pressures of up to 7 MPa. The physicochemical properties associated with the separation function are characterized by pore size, surface morphology or roughness, surface charge, and hydrophobicity (Bellona et al. 2004). Retention of compounds is based on solute-membrane interaction mechanisms, namely, steric hindrance, electrostatic repulsion for charged solutes, and hydrophobic-hydrophobic and dipole-dipole interactions. The transport mechanism for RO membranes can be described by the widely accepted solution-diffusion model (Wijmans and Baker 1995).

Challenges for RO Membrane Desalination

The commercially available TFC RO membranes have excellent salt retention properties, typically greater than 99.5 % (Baker 2004). However, boron removal, which is usually less than 95 %, is a major challenge to RO membranes to meet the recommended value of below 0.5 mg/L in drinking water by the World Health Organization (Jonsson and Macedonio 2010; Misdan et al. 2012). Boron exists naturally in seawater

High-Rejection Seawater Reverse Osmosis Membrane,

Fig. 1 Structure of composite RO membrane (Uemura et al. 2012)



(pH 7–8) in the form of uncharged boric acid with pKa value of 9.2 and at concentration of ~ 5 mg/L. Below pH 9, the non-hydrated boric acid is poorly rejected due to the lack of electric double layer repulsive force between the negatively charged membrane surface and boric acid. Current practice for boron removal in seawater desalination is either to install a second pass RO or ion exchange column to further purify the water or to increase the pH to above 9 so that the membrane can easily reject the hydrated boric acid. The latter is least preferred as it can promote membrane scaling by hardness in the water.

Another concern is the incomplete retention of trace organic micro-pollutants such as endocrine-disrupting compounds, pesticides, pharmaceutically active compounds, etc. (Bellona et al. 2004). In general, due to the nature of the membrane, charged/hydrophilic molecules have better retention than uncharged/hydrophobic molecules. However, predictive models to account for the organic solute transport through the membrane are still lacking.

In addition, true retention is an intrinsic property of the membrane, though the observed retention is strongly influenced by the process parameters such as operating pressure, temperature, pH, and membrane fouling. For instance, when a membrane is fouled, the solutes no longer freely move in the concentration polarization boundary layer, instead need to diffuse through the tortuous paths in the fouling layer. Consequently, the hindered back-diffusion effect causes greater accumulation of solutes at the membrane

wall, thus resulting in the increase of solute passage (Fane et al. 2009). Hence, a high-retention membrane needs to possess good antifouling properties to ensure consistent performance in long-term operation.

Future Direction

Incorporation of nano-materials and biomaterials into the active layer is seen to be the innovative way to produce the next generation of high-permeability and high-retention seawater RO membranes, i.e., nanocomposite or biomimetic membranes (Matsuura and Fane 2013). In addition, a thorough understanding on the molecular structures of membrane and its interaction with solutes via molecular simulation is necessary to allow better manipulation of surface properties such as the extent of cross-linking, chain-packing density, and chain stiffness in order to enhance the performance of RO membranes.

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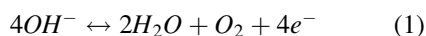
High-Temperature Electrolysis

César Valderrama

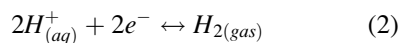
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High-temperature electrolysis (also called steam electrolysis) is the water electrolysis at temperatures that ranged between 700 and 1,000 °C in which electrical energy is the driving force of water splitting to produce oxygen (O₂) and hydrogen (H₂). The core of an electrolysis unit is an electrochemical cell, which is filled with pure water and has two electrodes connected with an external power supply. At a certain voltage, which is called critical voltage, between both electrodes, the electrodes start to produce hydrogen gas at the negatively biased electrode (Eq. 1) and oxygen gas at the positively biased electrode (Eq. 2). The amount of gases produced per unit time is directly related to the current that passes through the electrochemical cell (Wendt and Kreysa 1999).

Oxygen and hydrogen gas can be generated at noble metal electrodes by the electrolysis of water: positive electrode (anode):



negative electrode (cathode):



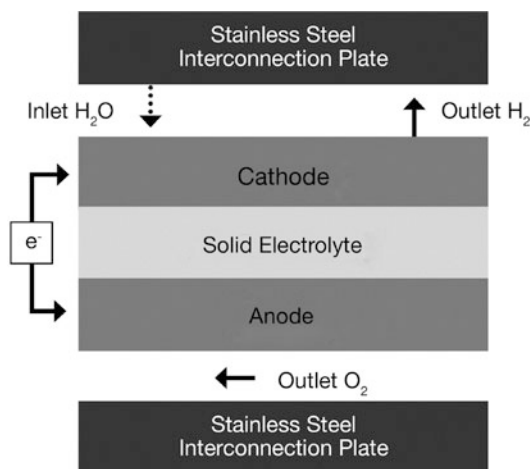
From the thermodynamic viewpoint of water decomposition, it is more advantageous to electrolyze water at high temperature (800–1,000 °C) because the energy is supplied in mixed form of electricity and heat. The main advantage is that a substantial part of the energy needed for the electrolysis process is added as heat, which is much cheaper than electric energy. In addition, the high temperature accelerates the reaction kinetics, reducing the energy loss due to electrode polarization, thus increasing the overall system efficiency (Zoulias et al. 2004).

The minimum necessary cell voltage for the start-up of electrolysis, E_{cell}^0 , is given under standard conditions (P, T constant) by the following equation (Allebrod 2013):

$$E_{cell}^0 = \frac{-\Delta G^0}{nF}$$

where ΔG^0 is the change in the Gibbs free energy under standard conditions, n is the number of electrons transferred, and F is the Faraday constant. The overall water electrolysis cell reaction, E^0 (25 °C), is 1.23 V, the Gibbs free energy change of the reaction is +237.2 kJ/mol, and the standard reaction enthalpy is $\Delta H^0 = 285.8$ (kJ/mol). The water splitting is an endothermic reaction, and the term ΔG decreases with increasing temperature (Zeng and Zhang 2010).

Thermodynamic conditions of high-temperature electrolysis are more favorable in the sense that the molar Gibbs energy of the reaction (ΔG) drops from ~1.23 V (237 kJ/mol) at ambient temperature to ~0.95 V at 900 °C (183 kJ/mol), while the molar enthalpy of the reaction (ΔH) remains essentially unchanged ($\Delta H \sim 1.3$ V or 249 kJ/mol at 900 °C) (Larminie and Dicks 2003). A significant part of the energy required for an ideal (loss free) high-temperature electrolysis can thus be provided by heat. Thus, these systems can utilize waste heat from nuclear (especially fast breeder reactors), chemical, and



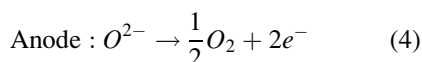
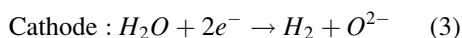
High-Temperature Electrolysis, Fig. 1 A schematic of solid oxide electrolysis cell (SOEC) for high-pressure electrolysis (Brisse et al. 2008)

coal- or natural gas-fired power plants and reduce the electric power requirements. Alternatively, the heat may come from solar concentrators, where high temperatures (above 800 °C) can easily be achieved.

Steam electrolysis or vapor electrolysis is performed using solid oxide electrolysis cell (SOEC) as shown in Fig. 1. This may be viewed in simple terms as the reverse operation of a solid oxide fuel cell.

The stream passes through the cathode side of the solid electrolyte where hydrogen ions are reduced to hydrogen, releasing oxide ions in the process (Eq. 3). The oxide ions then migrate through the electrolyte to the anode where they combine to form oxygen molecules (Eq. 4), releasing an electron current following back to the power source (Zeng and Zhang 2010).

The reactions on two electrodes are:



There are a number of materials that are used for the fabrication of electrolyzers that operate above 500 °C. The electrolyte is typically an oxide

ceramic and conducts either oxide ions or protons. Such systems are typically known as solid oxide electrolysis cells (SOEC). Material choice for the electrodes and operating temperature is essentially defined by the composition and type of the electrolyte material used with all other components being matched to the electrolyte. The conductivity of the electrolyte is a key parameter as it is a large contributor to cell losses and defines the design and operating temperature regime of the electrolysis cell.

The most widely studied high-temperature electrolyzers are based on O²⁻-conducting ceramics such as fully or partially stabilized (with Y₂O₃, Sc₂O₃) zirconia (referred to as YSZ or ScSZ). The advantages of these electrolyzers are that they can be incorporated with low-grade waste heat from chemical or power plants or solar thermal energy to reduce the electrical power input and increase efficiency; however, severe limitations on construction materials; significant problems with system design, materials' degradation, and lifetimes; hydrogen production on the anode side of the cell leading to complex system design; slow start-up and shut-down; and limited thermal cycling capability are disadvantages of these conducting systems (Badwal et al. 2013).

Apart from O²⁻-conducting electrolytes, several proton-conducting systems have been studied for the electrolysis of steam. In these systems, pure hydrogen is produced on the cathode side of the electrolysis cell with the oxygen being produced in the anode chamber where steam is present. Proton conduction in perovskite-structured SrCeO₃, where Ce is partially (5–10 %) substituted by Y, Yb, Mg, or Sc, was first developed and used for steam electrolysis in the 1980s. Following this early work, a number of other materials (based on BaCeO₃, CaZrO₃, SrZrO₃, and BaZrO₃) have been investigated, and their performance in steam electrolysis cells evaluated. Hydrogen is produced on the cathode side that simplifies system design, but in addition to the disadvantages of O²⁻-conducting systems, very few electrolytes offer good proton conductivity and stability in the operating regime (Badwal et al. 2013).

Hydrogen production via steam electrolysis may involve less electrical energy consumption than conventional low-temperature water electrolysis, reflecting the improved thermodynamic and kinetic operating conditions at elevated temperatures. For an average current density of $7,000 \text{ A}\cdot\text{m}^{-2}$ and an inlet steam temperature of $1,023 \text{ K}$, the predicted electrical energy consumption of the stack is around 3 kWh per normal m^3 of hydrogen, which is significantly smaller than 4.5 kWh of low-temperature alkaline water electrolysis cells commercially available today (Zeng and Zhang 2010). However, this result does not include the heating energy circulation and loss. Furthermore, construction materials, safety issues, and strict temperature control have to be addressed as well. Typical high-temperature electrolyser achieves 92 % electrical efficiency, while low-temperature electrolyzers can reach at most 85 % efficiency (Zoulias et al. 2004). Despite this high efficiency with respect to electricity, the high-temperature system still produces hydrogen at about four times the cost of the steam reforming hydrogen.

Intermediate-temperature electrolysis: A number of proton and O_2 —conductors are available for potential use as the solid electrolyte for water electrolysis in the 100 – 500°C temperature range. The perfluorosulfonic acid polymer membrane-based electrolyzers (PEM) are generally not operated above 90°C due to a reduction in proton conductivity caused by its dehydration. Approaches used to increase the operating temperature range of polymer membranes (fuel cells and electrolysis cells) include the use of Polybenzimidazole (PBI)/acid complex membranes, hybrid membranes consisting of polymers, and proton-conducting oxides and composite membranes consisting of ceramic particles (SiO_2 , TiO_2 , etc.) impregnated proton-conducting membranes. Mainly, SiO_2 - or TiO_2 -impregnated perfluorinated polymer-based composite membranes (cells with 1 – 5 cm^2 active area) have been employed in investigations for temperatures up to 130°C (Badwal et al. 2013; Baglio et al. 2009; Xu et al. 2011).

Cross-References

► Hybrid Membranes

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High-Throughput Membrane Technology

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The term “**high-throughput**” (HT) refers to the creation of a large output, i.e., a large amount of data that is obtained from simultaneous, parallel experiments. In general, HT methodologies are used to speed up the formulation and discovery

of new materials or the optimization of processes. They include a variety of advanced tools which allow fast parallel experiments, leading to higher productivities and shorter “time to market” times. While “HT” thus refers to the number of experiments, “combinatorial” strategies are related with the experimental design.

Besides automation (to whatever desired degree), a faster screening and more rapid optimization due to simultaneous testing, other **advantages** of HT technologies are the miniaturization (leading to smaller sample sizes and reductions in costs and waste streams) and the reproducible conditions between samples (as parallel tests are performed under identical experimental conditions, e.g., pressure, temperature).

Membrane technology can gain from the implementation of HT technologies on several levels. As membrane performance is influenced by a variety of parameters, an efficient HT screening of multiple variables can lead to the rapid development of new membranes and membrane applications.

HT devices can be implemented during the **membrane preparation**, the membrane screening, and the optimization of the membrane process parameters. The former relates to automated devices developed for weighing powders, dispensing liquids, homogenizing solutions, casting these polymer solutions, dip coating, etc. More details can be found on www.html-membrane.beand, www.porometer.com.

HT devices for **membrane screening** are commercially available for pressure-driven **liquid** separation systems with a variable number of membranes and different membrane areas per equipment (Vandezande et al. 2005; Cano-Odena et al. 2011; Van Doorslaer et al. 2010; www.porometer.com 2014). Commercially available HT devices also exist for **gas** separations, which were successfully applied to perform quality control tests at industrial-scale production and to quickly analyze membrane performance in diverse studies (Khan et al. 2010, 2013; Basu et al. 2011). The development of an HT membrane **bioreactor** (MBR) was also reported to simultaneously study the performance and fouling

properties of multiple membranes in one aerated MBR (Bilad et al. 2011). In addition, an HT cross flow filtration system was adapted into an online **fouling monitoring** system, allowing fouling studies of multiple membranes with high-quality imaging and a high reproducibility (Vanysacker et al. 2013). **Filter plate HT platforms** were also applied together with photoinduced graft polymerization or atmospheric pressure plasma-induced graft polymerization to synthesize and screen antifouling membranes (Zhou et al. 2009; Gu et al. 2013). An HT ionic conductivity apparatus and an HT mechanical testing apparatus for thin membranes were also reported (Zapata et al. 2009, 2010).

When new HT devices are developed, their **performance** should be evaluated based on their reproducibility (of the same sample), interchangeability (of sample positions), and scalability of the setup (compared to conventional methods) (Bilad et al. 2011).

Together with the application of HT technology, the **design of experiments** (DoE) has become increasingly important. As membranes can now be quickly synthesized and screened, the implementation of appropriate experimental design is crucial to obtain membranes with optimal performances. The aim is then to quickly eliminate experimental areas in which limited successes are expected so combined experimentation can be focused on potentially promising areas. An efficient search strategy combined with HT technology can rapidly lead to an optimum in a large parameter space, in contrast to the slower and less effective traditional parameter-by-parameter approach. Two important aspects are the certainty of finding an optimum and a rapid progression of convergence toward the optimal membrane performance.

Several experimental design types were already applied in membrane technology. Among them are artificial neural networks (ANNs) to predict membrane fouling and separation performances in both liquid and gaseous environments (Soleimani et al. 2013; Shokrian et al. 2010). Genetic algorithms (GAs) were applied to obtain an optimum in membrane

composition, separation modules and operating conditions, gas separation systems, and desalination units (Bulut et al. 2006; Vandezande et al. 2009; Yuen et al. 2000; Chang and Hou 2006; Guria et al. 2005). Genetic programming, Plackett-Burman design, Taguchi's method, response surface methodology, and fractional factorial design are other DoE types already employed in membrane technology.

The combination of HT technology with appropriate DoE clearly leads to the acceleration of acquiring output, hence, to a better understanding of the effects of parameters and the properties of new membrane materials and formulations. It can thus generate a significant decrease in cost and increase in efficiency during the discovery and optimization stages of membrane design and development processes.

Cross-References

► Design of Experiment (DOE)

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Hollow Fiber

Khayet Mohamed

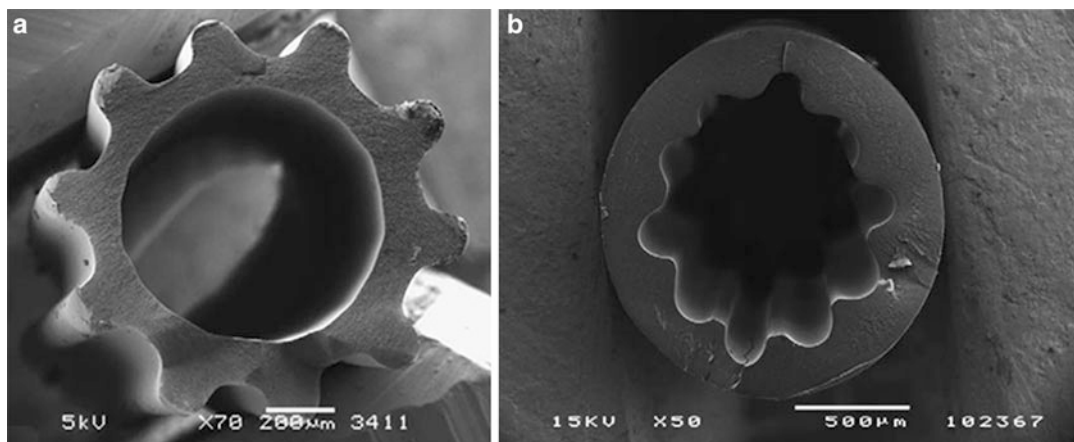
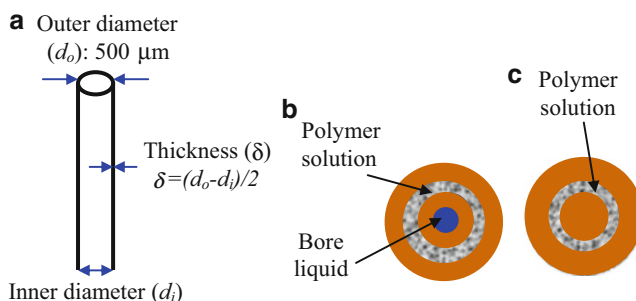
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In general a hollow fiber is a cylindrical geometry of any material having a hollow space with an external diameter approximately less than 0.5 mm (Fig. 1). It may have different cross-sectional shapes such as round, trilobal, pentagonal, octagonal, etc. Both smooth and corrugated-shaped hollow fibers were fabricated from different micro-engineered or smart spinnerets (Fig. 2). Various types of spinnerets (i.e., single or dual spinnerets, straight annular or conical spinnerets, microstructured orifice in

spinneret) with different configurations and dimensions are used in spinning hollow fibers (Khayet and Matsuura 2011). The difference between capillary, tubular, and hollow fiber is simply a matter of dimensions. The approximate diameter of a capillary membrane is between 0.5 and 5 mm, while that of a tubular membrane is higher than 5 mm (Mulder 1992). Since hollow fibers are mechanically self-supporting, the fiber dimensions are very important. A hollow fiber has an inner diameter (d_i) and outer diameter (d_o), while the thickness (δ) of the hollow fiber wall is the difference between the outer radius and the inner radius. The primary process variables establishing hollow fiber diameters and thickness are spinneret geometry. Other spinning parameters such as the bore liquid (fluid) flow rate, the dope extrusion rate, the take-up velocity and the air gap distance can modify the geometrical

Hollow Fiber,

Fig. 1 Hollow fiber (a) and cross-section of common spinnerets (b, c) used for fabrication of hollow fibers by (a) wet spinning and dry/wet spinning and (b) melt spinning and dry spinning



Hollow Fiber, Fig. 2 Scanning electron microscopy (SEM) images of polyethersulfone/polyimide (PES/PI) blend hollow fiber membranes with a corrugated outer (a)

and inner (b) microstructure (Reprinted from (Nijdam et al. 2005). Copyright 2005, with kind permission from Elsevier)

parameters of the spun hollow fibers. For example, Wu et al. (2007) found that the thickness of the poly(vinylidene fluoride), PVDF, hollow fibers prepared by wet spinning technique decreased with the increase of the internal coagulant (bore liquid) flow rate. For example, when the bore liquid flow rate was increased from 1.1 to 1.5 ml/min and further to 1.8 ml/min, the corresponding thickness of the PVDF hollow fibers decreased from 188 to 176 μm and further to 155 μm . An enhancement of the inner diameter and a reduction of the outer diameter of the hollow fibers with the increase of the bore liquid flow rate were detected.

The process of fabricating synthetic hollow fiber membranes is more difficult than that of flat sheet membranes. In general, the process is carried out by extruding or pumping a dope solution through a spinneret (Fig. 1) following different methods such as melt spinning, dry spinning, wet spinning, or dry/wet spinning. In melt spinning and dry spinning, the dimensions of the spinneret are not so crucial because the fiber dimensions are mainly determined by the ratio of the extrusion rate and “tearing rate” (Khayet and Matsuura 2011). In wet spinning and wet/dry spinning, the spinneret has a tube-in-orifice structure with typical dimensions 0.5–1 mm inner diameter and 0.9–2 mm outer diameter.

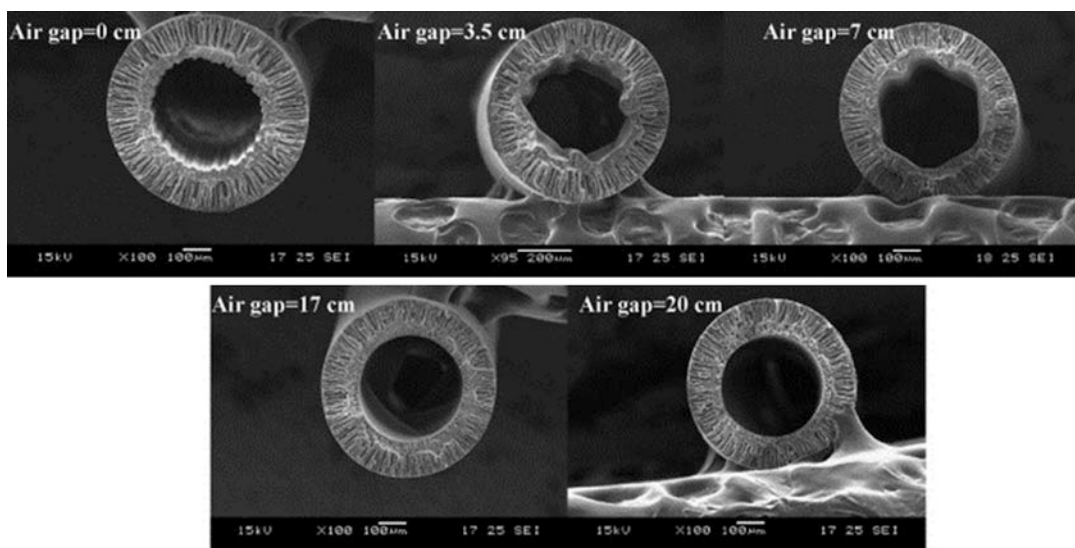
The first hollow fiber membranes were patented by Mahon in late the 1960s (Mahon 1966a, b). Various types of hollow fiber membranes, hydrophobic or hydrophilic, dense or porous, single or double layered, have been proposed for different membrane separation processes leading to a fast growth of synthetic membrane technology. Since then significant efforts have been made to develop new hollow fibers with desirable structures and morphologies. However, until now, various scientists admit that understanding the mechanisms of hollow fiber formation is rather qualitative than quantitative. It is not easy to control the characteristics of hollow fibers because various important spinning parameters are involved simultaneously. For example, the preparation of the hollow fiber membrane by the dry/wet spinning or wet spinning techniques requires both internal (bore liquid)

and external coagulants and involves more controlling parameters than the flat sheet membrane. Shape and dimension of the spinneret, viscosity of the spinning dope (whether hollow fibers can be spun from the dope), temperature of the spinning dope, properties of the internal and external coagulants, flow rate of the bore liquid, dope extrusion rate, length and humidity of the air gap, wind-up speed, and fiber take-up speed are some of those examples. As a consequence, the major parts of hollow fibers that appeared in the literature with different structures and morphologies are based mostly on trial-and-error experiments.

Hollow fibers are mechanically self-supporting, have good flexibility, and are easy to assemble in module and to handle for different applications. The feed is supplied to either the inside or outside of the fiber, and the permeate passes through the fiber wall to the other side of the fiber. The fiber wall may have an asymmetric structure being the active skin layer placed to the feed side. A bundle of hollow fibers are often mounted in a shell and tube module, which is featured by a very large packing density (i.e., high surface area per unit module volume), and therefore the size of the hollow fiber module is smaller than other modules for a given performance capacity. The packing capacity of a hollow fiber module may reach 500–9,000 m^2/m^3 resulting in a high productivity per unit volume.

Spinning corrugated hollow fibers is similar to spinning smooth cylindrical fibers; the only difference is the use of a modified spinneret (Cao et al. 2004; Çulfaz et al. 2010; Nijdam et al. 2005; Wang et al. 2004). For example, to prepare a hollow fiber with a corrugated inner microstructure instead of a cylindrical needle, the spinneret is fabricated with a structured needle. To spin a hollow fiber with a corrugated outer surface, a microstructured orifice is incorporated to the spinneret. Figure 2 shows SEM images of corrugated hollow fiber membranes.

The use of corrugated membrane surfaces is to enhance the heat and mass transfer by increasing the membrane surface area and the turbulence near the membrane surface. Corrugations act as turbulence promoters but also may lead to an increase of pressure drop in the flow channel. It



Hollow Fiber, Fig. 3 Cross-sectional structure of PVDF hollow fiber membranes prepared with wet spinning technique and dry/wet spinning technique using 20 wt.% PVDF in the solvent N-methylpyrrolidone (NMP) and

40 wt.% NMP aqueous solution as internal coagulant (Reprinted from (Bonyadi et al. 2007). Copyright 2007, with kind permission from Elsevier)

was observed that the size of the corrugations on the fiber was very sensitive to the air gap length and even disappeared from the external surface for high air gap lengths. When used in gas separation, the selectivity (oxygen/nitrogen) and permeance of polyethersulfone/polyimide (PES/PI) blend corrugated hollow fiber membrane were found to be similar to those of smooth cylindrical fibers (i.e., circular-shaped fibers) prepared under the same operating conditions. However, the gas permeate flow was increased by 19 %, which is the increase of membrane surface area due to corrugations (Nijdam et al. 2005). It is worth quoting that an increase of membrane surface area of 89 % can be obtained with a corrugated hollow fiber membrane (Çulfaz et al. 2010). Furthermore, PES/PVP blend hollow fiber membranes were used in *UF*, and it was found that the water permeability, molecular weight cutoff, and pore size distribution of both the corrugated and circular-shaped fibers were similar (Çulfaz et al. 2010). This indicates a higher permeate flow of the corrugated hollow fiber compared to the circular-shaped fiber and a similar *UF* separation factor.

Instabilities and irregularities may occur during hollow fiber spinning inducing corrugations at

their external or internal contours. These corrugations can be eliminated increasing the air gap distance (Fig. 3). The number of corrugations in the internal surface of the hollow fiber membranes is reduced approaching a final circular shape. The hydrodynamic instability, which leads to nonuniform cross-section and wavy geometry, might be due to the pressure induced in the nascent fiber (as a result of diffusion/convection, precipitation, densification, and shrinkage), which will buckle the rigid elastic shell formed at the interface between the bore fluid and the spinning dope solution (Bonyadi et al. 2007).

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Hollow Fiber Carbon Molecular Sieve Membranes

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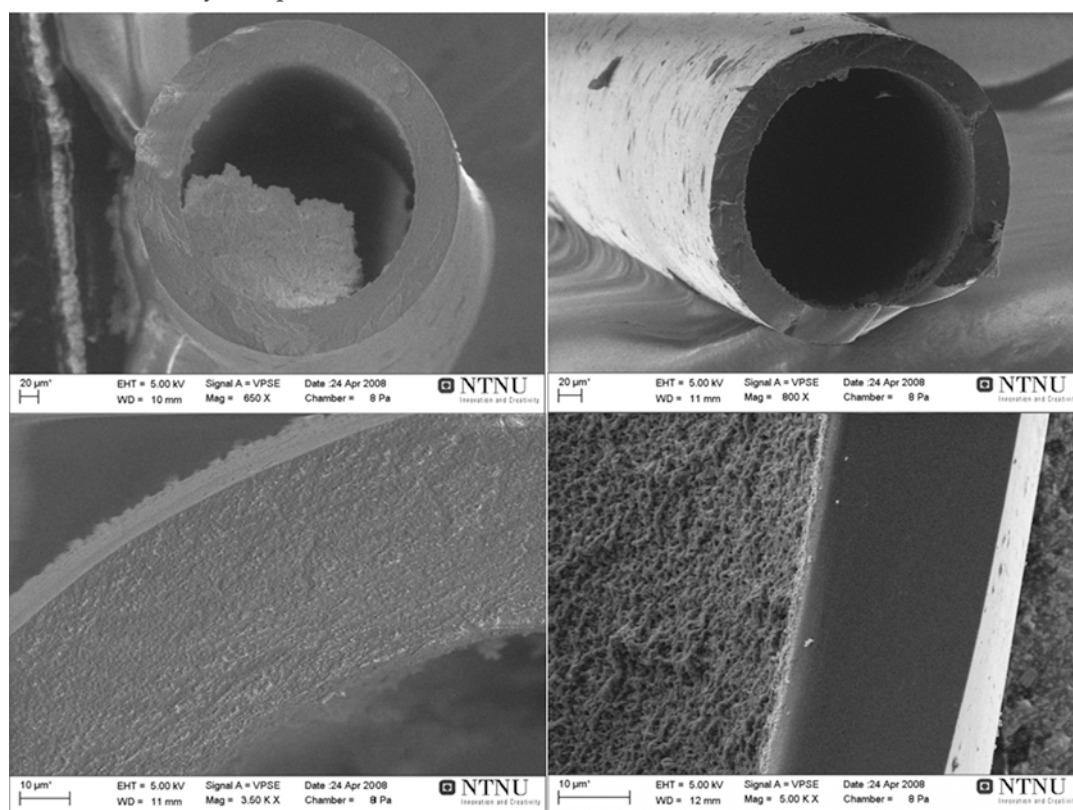
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Carbon molecular sieve (CMS) membranes have been studied in more than twenty years as promising and energy-efficient membranes for gas separation. Due to their high permeability, selectivity, and also thermal and chemical stability under adverse and harsh conditions, the CMS membranes are becoming increasingly important for separating gas mixtures with quite similar molecular kinetic diameter. Carbon molecular sieve

H

Deacetylated precursor-2h

Carbon membrane-HFCM-2



Hollow Fiber Carbon Molecular Sieve Membranes, Fig. 1 SEM images of cross section of precursor and HFCM-2. (a, c) are the cross section of the precursor; (b, d) are the cross section of the prepared carbon membrane (He et al. 2011)

Hollow Fiber Carbon Molecular Sieve Membranes, Table 1 Structural parameters of the cellulosic-based carbon membranes (He and Hägg 2012)

Carbon membranes	True density, ρ_s (g cm^{-3}) ^a	Bulk density, ρ_b (g cm^{-3})	W_0 ($\text{cm}^3 \text{g}^{-1}$)	E_0 (kJ mol^{-1})	Average micropore width ($\text{\AA}$)	Reference
HFCM-1	1.53	1.24	0.15	32.2	5.2	This work
HFCM-2	1.38	1.12	0.17	30.8	5.6	This work
CMSM1	1.6	1.1	0.28	31.6	5.5	(Lagorsse et al. 2004)
CM-V823			0.16	22.75		(Lua and Su 2006)

^aDensity of carbons is 1.3–1.8 g cm^{-3} as compared to 2.2 g cm^{-3} for graphite (Koresh and Soffer 1983)

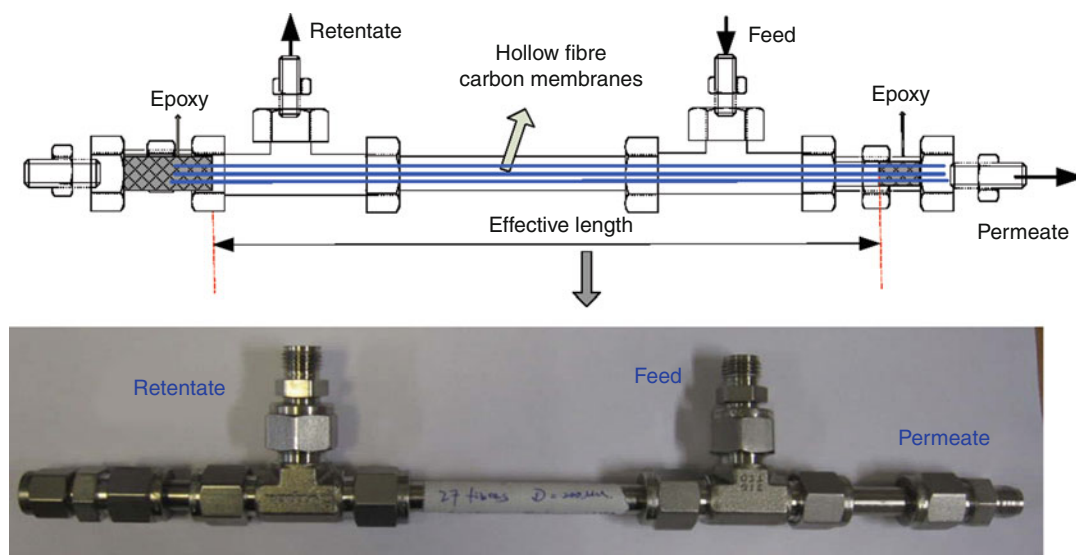
membranes can be prepared by controlling the carbonization procedure during carbonization of different polymeric materials such as polyimide, polyacrylonitrile (PAN), phenolic resin, poly(phthalazinone ether sulfone ketone), poly(phenylene oxide), cellophane paper, cellulose, and deacetylated cellulose acetate. The carbonization parameters (e.g., purge gas, purge gas flow rate, final temperature, heating rate, and final soak time) will affect the resulting carbon membrane performance, and the optimal condition was obtained on the basis of experimental design and statistical analysis to prepare the high-performance carbon membranes for a specific application as reported by He et al. (He and Hägg 2011a). Different techniques such as scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) have been used to characterize the membrane's structure and morphology. Figure 1 shows the cross section and inside surface of the precursors and HFCMs, respectively (He et al. 2011). The outer diameter and wall thickness of the HFCMs were approximately 250 μm and 30 μm , respectively, indicating a significant radical shrinkage comparing to the precursor membranes with 400 μm and 50 μm .

The pore size and pore-size distribution (PSD) can be estimated by gas gravimetric adsorption measurements equipped with a Rubotherm magnetic suspension balance (MSB) (Belmabkhout et al. 2009). The structural parameters of a cellulosic-based carbon membrane have been estimated from CO_2 sorption measurements, and a narrow pore-size distribution was found by He

et al. (He and Hägg 2012), and the results were shown in Table 1, which will be helpful to understand the transport mechanism through carbon membranes.

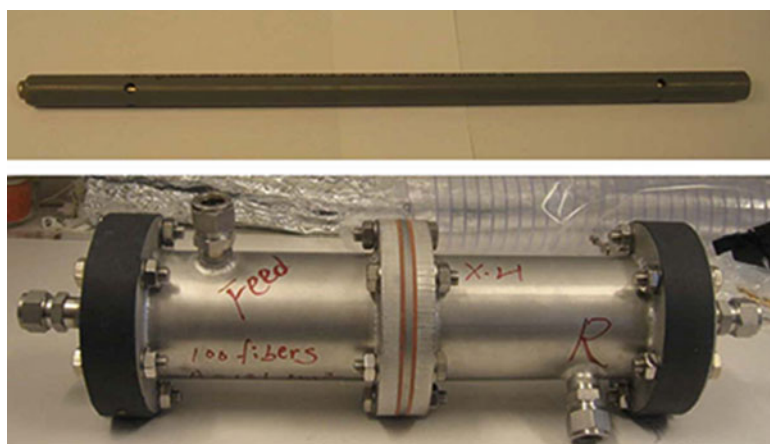
The operating parameters such as feed pressure, temperature, and flow rate of retentate will greatly affect the CMS membrane separation performances and need to be optimized for a specific application as reported by He et al. (He and Hägg 2011b). Considering the aging problem for most carbon membranes, different regeneration techniques can be used to recover the performances online or off-line (Lie 2005; Hagg and He 2011). In order to ensure the efficiency of the carbon membrane separation process, a hollow fiber membrane module should be designed and constructed. Figure 2 shows a schematic and lab-scale hollow fiber carbon membrane module (He and Hägg 2011b), while Fig. 3 shows a small pilot-scale module (designed by one of NanoGloWa project partner, HyGear B.V.) (He 2011). Single-gas permeability tests at different temperatures and pressures were mostly conducted by using the lab-scale module, while the small pilot-scale module was employed to test the gas mixture at a higher permeate flux in order to determine the gas composition more precisely.

Based on the experimental investigations and process simulations, the carbon membranes show high potential for selected industrial applications such as CO_2 - CH_4 separation for biogas upgrading (Hägg and Lie 2006), H_2 - CH_4 separation wherever relevant (Grainger and Hägg 2008), and CO_2 capture from flue gases (He and Hägg 2011b; He et al. 2009). Moreover, carbon molecular sieve



Hollow Fiber Carbon Molecular Sieve Membranes, Fig. 2 A schematic and lab-scale carbon membrane module (He and Hägg 2011b)

Hollow Fiber Carbon Molecular Sieve Membranes, Fig. 3 A small pilot-scale carbon membrane module (Designed by HyGear) (He 2011)



membranes also show a great potential in air separation, petrochemical, and high-temperature membrane reactor applications.

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should be considered: flow in lumen, within membrane matrix, and in the extracapillary space (Nagy 2011, p. 179). Let us consider a steady-state, laminar, incompressible, isothermal, fully developed flow in vertically oriented tube; thus the Navier-Stokes equations (Bird et al. 1960) will be as the continuity equation:

$$\frac{1}{r} \frac{\partial}{\partial r}(rv_r) + \frac{\partial u}{\partial z} = 0 \quad (1)$$

where u is the axial convective velocity, m/s; v_r is the transverse convective velocity, m/s; and z is the axial space coordinate, m. The momentum equations are as

$$\begin{aligned} \rho \left(v \frac{\partial u}{\partial r} + u \frac{\partial u}{\partial z} \right) = & -\frac{\partial p}{\partial z} \\ & + \mu \left\{ \frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial(ru)}{\partial r} \right] + \frac{\partial^2 u}{\partial z^2} \right\} \end{aligned} \quad (2)$$

$$\begin{aligned} \rho \left(v \frac{\partial v}{\partial r} + u \frac{\partial v}{\partial z} \right) = & -\frac{\partial p}{\partial r} \\ & + \mu \left\{ \frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial(rv)}{\partial r} \right] + \frac{\partial^2 v}{\partial z^2} \right\} \end{aligned} \quad (3)$$

and for solute concentration in case of constant density

$$\begin{aligned} u \frac{\partial c}{\partial z} + v \frac{\partial c}{\partial r} = & \frac{\partial}{\partial r} \left(D \frac{\partial c}{\partial r} \right) + \frac{1}{r} \frac{\partial(Dc)}{\partial r} \\ & + \frac{\partial}{\partial z} \left(D \frac{\partial c}{\partial z} \right) \end{aligned} \quad (4)$$

where ρ is the density, p is the pressure, μ is dynamic viscosity, and g is gravitational acceleration.

Equations 2 and 3 may be reduced by considering the fact that for a small wall Reynolds number, the inertial terms can be negligible. In most viscous flows, normal stress effects, $\partial^2 u / \partial z^2$, are negligible when the ratio, r_o/L (L is length of capillary, r_o is lumen radius), is less than 10^{-2} , a condition that is satisfied in almost all hollow fiber membrane

Hollow Fiber Enzymatic Reactor, Modeling of

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Modeling of hollow fiber enzymatic reactor.

The complete description of the transport of fluid in hollow fiber capillary membrane requires that the local transport equations that describe the flow and transport conditions should be solved. The starting Navier-Stokes flow models (Bird et al. 1960) are very complex; significant simplification is needed to obtain applicable model for engineering points of view. In a capillary membrane with permeable wall, three regions of flow

devices. Depending on the transmembrane convective velocity, the axial velocity often can be much larger than that of the permeation rate. Due to its large values, the axial diffusion term can be neglected. The radial convective velocity is rather low; accordingly, momentum equation of the transverse velocity can be neglected. Accordingly, Eqs. 2 to 4 can be simplified as

$$0 = -\frac{\partial p}{\partial z} + \mu \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u}{\partial r} \right) \quad (5)$$

The component balance will be as:

$$u \frac{\partial c_i}{\partial z} = D \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) \quad (6)$$

When Eq. 6 is integrated twice with respect to r , one can get as

$$u = \frac{dp}{dz} \frac{r^2}{4} + A \ln r + B \quad (7)$$

For the hydrodynamic analysis in the lumen and in the shell, the continuity Eq. 1 and the momentum Eq. 5 have to be solved with suitable boundary conditions. In the lumen (t) these are

$$\text{at } r = 0 \text{ then } \frac{\partial u}{\partial z} = 0, \quad v = 0; \quad (8)$$

$$\text{at } r = r_0 \text{ then } v = 0 \quad (9)$$

Consequently it can be get

$$u = -\frac{r_o^3}{4\mu} \left(1 - \left[\frac{r}{r_o} \right]^2 \right) \frac{dp_t}{dz} \quad (10)$$

Replacing Eq. 10 into Eq. 5, one can get for the radial convective velocity in the lumen side (for distinction for the membrane's velocity, f subscript denotes the fluid phase here in the lumen side)

$$v_t = \frac{r_o^3}{\mu 8} \left\{ \frac{r}{r_o} - \frac{1}{2} \left(\frac{r}{r_o} \right)^3 \right\} \frac{d^2 p_t}{dz^2} \quad (11)$$

From Eq. 11 the wall velocity, v_w , can be given as

$$v_w = \frac{r_o^3}{16\mu} \frac{\partial^2 p_t}{\partial z^2} \quad (12)$$

The radial convective velocity through the membrane can also be expressed by the next equation

► **Biocatalytic membrane reactor: mass transport** as

$$v_M(r, z) = \frac{\kappa}{\varepsilon \mu} \frac{r_o}{r} \frac{p_t(z) - p_e(z)}{\ln(1 + \delta/r_o)} \quad (13)$$

From equality of Eqs. 12 and 13, a second-order differential equation can be obtained neglecting the radial pressure gradient (Nagy 2011, p. 187). Solving this equation the $p(z)$ and $v_w(z)$ functions can be obtained (Nagy 2011). This convection velocity can then be replaced in the mass balance equation for the membrane (see “► **Biocatalytic Membrane Reactor, Mass Transport** in).

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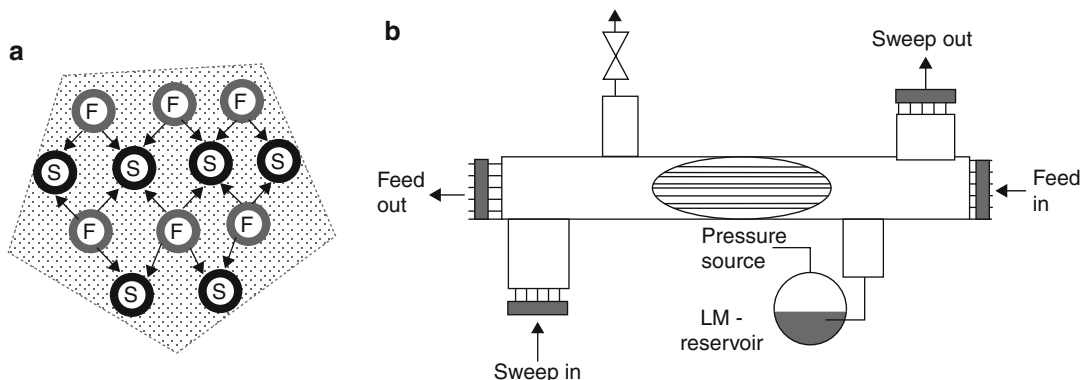
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Hollow Fiber Liquid Membrane

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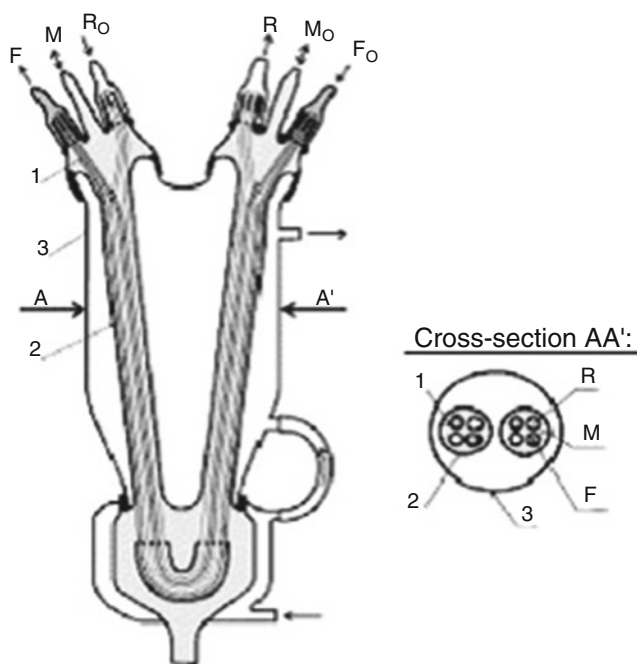
Hollow fiber (HF) supported liquid membrane is a three-phase liquid membrane system in which the membrane phase (liquid) is held by capillary forces in the pores of microporous polymeric or inorganic hollow fibers. The design of the hollow fiber SLM module consists of a certain number of thin fibers, placed along the length of the shell. The feed phase is pumped through the fibers; the



Hollow Fiber Liquid Membrane, Fig. 1 Hollow fiber contained liquid membrane (HFCLM): (a) configuration of permeator shell and (b) side view of the permeator

Hollow Fiber Liquid Membrane,

Fig. 2 Scheme of the hollow fiber contactor with parallel flow of phases distributed U-shaped bundles of fibers with separated inlet and outlet end chambers. [*F* feed (donor) phase, *M* liquid membrane phase, *R* stripping solution, 1 hollow fiber for the feed, 2 glass tubulet, 3 glass tempering jacket of the contactor] (From Schlosser and Sabolova 2002)



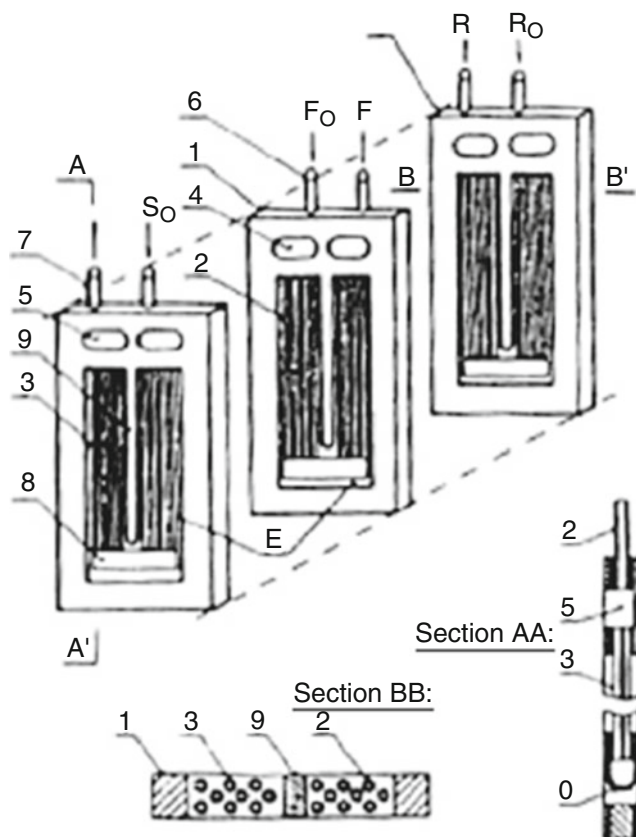
pores in the fibers are filled with the LM solution, and the receiving (strip) phase is forced out through the sides of the shell. HF SLMs are schematically presented in the Figs. 1, 2, and 3. Compact and modular hollow fiber devices can be used with exceptionally high mass transfer area per unit equipment volume. Very often such HF systems are termed as contactor devices. Contactor devices are used as construction units in many of the SLM, HFCLM, and BLM systems. The theory

of the HFLM transport was developed by Sirkar et al. (see in Sirkar 1996) and Schlosser et al. (see in Schlosser and Sabolova 2002).

Different hollow fiber modules can be classified into several groups. One, termed as a “hollow fiber contained liquid membrane (HFCLM)” (Majumdar and Sirkar 1992) configuration, is shown in Fig. 1a. The process is achieved by packing thousands of microporous hollow fibers in a permeator shell filled with stationary liquid

Hollow Fiber Liquid Membrane,

Fig. 3 Scheme of the hollow fiber contactor of three phases with crossflow of LM phase: (1) body of element, (2, 3) hollow fiber in downstream and upstream part, (4, 5) inlet and outlet chamber, (6, 7) inlet and outlet tube, (8) flowing head, (9) central baffle; *F* feed, *E* LM phase, *R* strip solution (From Schlosser 2000)



H

membrane solution. The fibers are present in feed and strip sets very close to each other but with the ends of each set being separated. If the fibers are hydrophilic, the aqueous feed and strip flow through the lumen side of the fibers and fill the pores of the fiber; if fibers are hydrophobic, they are wetted by organic LM phase (Fig. 1b). So, reader can see that this is a hybrid system with combination of modified SLM and BLM configurations.

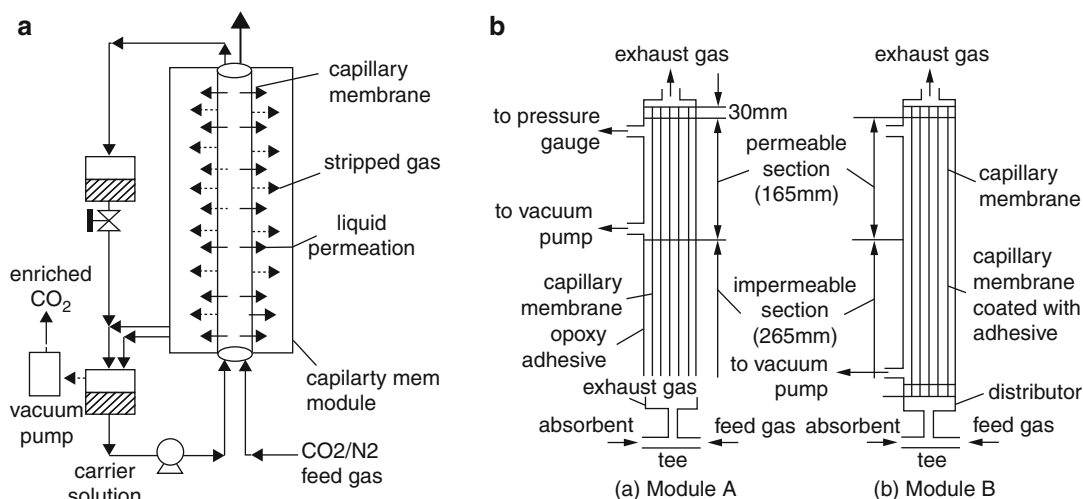
Hollow fibers in tube pertractor (Schlosser 2000) is another type of HF module (see Fig. 2) “with parallel flow consisting of one or two intermixed U-shaped bundles of microporous polypropylene fibers, inserted into polysulfon (or glass) tubes”. Pulsation of the LM phase along the fibers is used for better mixing.

One more type of the HF modules is presented schematically in Fig. 3. A crossflow with pulsation perpendicularly to fibers was used here. Some plate and frame HF modules were proposed. The

module with “fiber in fiber” units and crossflow of one phase is described in Ref. Schlosser and Sabolova (2002).

A capillary membrane module was developed (Teramoto et al. 2003) for gas separation. The concept of a capillary membrane apparatus is shown in Fig. 4. Both a feed gas and a LM solution are supplied to the lumen side (high-pressure feed side) of the capillary ultrafiltration membrane module and flow upward. The LM solution, which contains dissolved solute gas (CO_2), flows to the permeate side (low-pressure shell side), where the solution liberates dissolved gas to become a lean solution. The lean solution is returned to the lumen of the capillary module by a pump. In the shell side, dissolved gas is stripped from the liquid flowing down on the outer surface of the capillary and discharged from a vacuum pump through a liquid reservoir.

One more example of hollow fiber LM separation system is described as affinity dialysis (Devis



Hollow Fiber Liquid Membrane, Fig. 4 Schematic diagrams of facilitated transport of gas using capillary membrane module for removal and enrichment of carbon

dioxide: (a) experimental capillary membrane apparatus and (b) capillary membrane modules with permeation of carrier solution (From Teramoto et al. 2003)

et al. 1988) Water-soluble polymer (WSP) solutions as LM were immobilized into the pores of hollow fiber units (fibers of 5,000 molecular weight cutoff from Spectra/Por were used). Selective separation and concentration of both cations (Ca/Na, Cu/Zn) and anions (potassium chromate/sodium chloride) were tested. 2.5 % w/v aqueous solution of poly (2-acrylamido-2-methyl-1-propanesulfonic acid) (poly-AMPS) for cation separations and 5 % w/v solution of poly (ethylenimine) (PEI) for anion separations were used as LM. High concentration factor (50–75) and selectivity (30–40) were obtained.

Hollow fiber membrane catalytic reactors (HFMCr) and bioreactors (HFMBR) are relatively new developments of SLM techniques. The SLM reactors can be used to shift the equilibrium conversion (e.g., esterification reaction), to remove selectively products and by-products from the reaction mixture, and to supply selectively the reagents (e.g., oxygen for partial oxidation reactions) (Li et al. 2003). Application of SLM reactors appears of particular interest in hydrogen production and oxidation reactions. Applications of biocatalytic membrane reactors (Cussler and Ding 1995) provide an ideal support for catalyst immobilization due to their wide available surface area per unit volume and include

production of new or better foodstuffs, novel pharmaceutical products with well-defined enantiomeric compositions, conversion of lactose into glucose and galactose, the isomerization of glucose into fructose, and the separation of chiral isomers of acylated racemic amino acids and wastewater treatment.

The regeneration of degraded hollow fiber liquid membranes could be done by pumping the fresh LM at the lumen side of the support for a few minutes instead of the aqueous solution. Continuous impregnation of the membrane pores is possible as it is in the HFCLM devices or by adding membrane phase as an emulsion to the strip aqueous phases. It is termed the pseudoemulsion-based hollow fiber strip dispersion (PEHFSD) technique. The main drawback is pollution of the product with the membrane liquid.

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Hollow Fiber Membrane

► Hollow Fiber Membrane Module

Hollow Fiber Membrane Bioreactor for Cell Growth

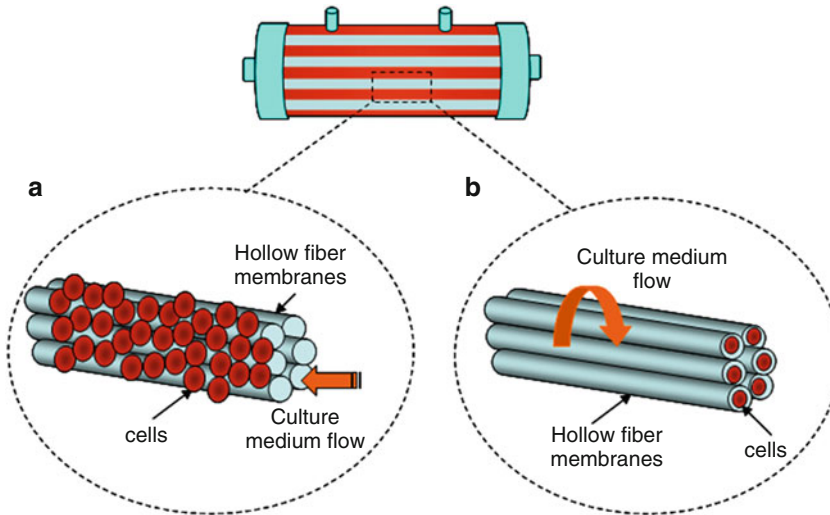
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Hollow fiber membrane bioreactor consists of hollow fiber membranes parallel-assembled in an external shell, which is usually in the shape of a cylinder. The fibers are potted in the shell, thus creating a medium and a cell compartment which

are separated by the membranes. Hollow fiber membranes of suitable MWCO separate cells from the medium compartment allowing the communication between the compartments through the pores of fiber wall. Depending on the pore sizes, the passage of nutrients, metabolites, and catabolites occurs and cells are retained. The principle of a hollow fiber bioreactor based on hemodialyzer modules was first described by Knazek (Knazek et al. 1972). Usually cells are cultured in suspension or attached to the outer surface of the membranes in the extracapillary space. Culture medium containing nutrients flows in the lumen of the fibers and diffuses out through the pores of the fiber wall to the cells. The metabolic species together with waste molecules produced by cells permeates back into the fibers and is removed from cell compartment (Fig. 1).

As bioreactors, they are extensively used for production of biochemicals and for the development of bioartificial organs. Recently they found applications in tissue engineering applications for the development of tissue constructs, cell therapy, and the expansion and transdifferentiation of stem cells. Hollow fiber bioreactor offers several advantages for the culture and growth of adherent and suspension cells including: (i) an in vivo-like microenvironment regarding nutrient supply and metabolic waste removal as each fiber replicates a blood capillary, (ii) high surface area to volume ratio, (iii) cells can be grown to high density, (iv) cells are protected from shear stress, and (v) support of three-dimensional growth of cells for the development of tissue-engineered constructs. Different types of polymers (polyethersulfone, polysulfone, polyacrylonitrile, modified polyetheretherketone, polyamide, cellulose acetate, etc.), generally hydrophilic polymers or with moderate wettability, are used for the development of hollow fiber bioreactors in order to favor the adhesion of cells or the exchange of medium. Hydrophobic hollow fibers (e.g., polypropylene) are included in some devices for a separate oxygenation of cells (Flendrig et al. 1997). A major drawback of the hollow fiber bioreactors is represented by the mass transfer resistance due to the membrane because while it separates cells from the medium compartment,



Hollow Fiber Membrane Bioreactor for Cell Growth, Fig. 1 Schematic diagram of hollow fiber membrane bioreactor used for cell culture and growth: (a) cells are cultured in the extracapillary space, and the medium

flows in the lumen of fibers; (b) cells are cultured in the lumen of fiber, and the medium flows in the extracapillary space

it does reduce diffusion of nutrients and oxygen to the cells. In addition, fouling due to the adsorption of plasma proteins or the development of biofilms further increases the resistance to mass transport. In the membrane bioreactors, mass transfer is determined by the MWCO or pore diameter of membrane and occurs by diffusion and/or convection in response to existing transmembrane concentration or pressure gradients. Most of the bioreactors use membranes with MWCO ranging from 70 to 100 kDa that allow the transport of small molecules that are fed or produced by cells but exclude proteins with high MW such as immunoglobulins and cells. These membranes provide immunoprotection, which is important when the devices are used in the organ replacement therapy in order to avoid the passage of immunocompetent species present in the patient's blood. Other bioreactors use microporous membranes with a large pore diameter ($0.2\ \mu\text{m}$) that permit the free passage of proteins, toxins, and clotting factors, but they exclude the passage of cells. The advantage of using a membrane with large pore diameter is that it increases the fluid convection improving the mass transfer conditions. Several hollow fiber membrane bioreactors

have been developed for the culture of cells that grow in adhesion and/or in suspension. Different configurations have been investigated for the culture and growth of primary cells (e.g., lymphocytes, hepatocytes, pancreatic islets, neurons, osteoblasts, fibroblasts), cell lines, progenitor cells, and stem cells (De Bartolo and Bader 2013). Usually cells are cultured in adhesion or suspension outside the fibers, and the medium flows in the lumen of fibers (De Bartolo et al. 2007a). In other bioreactors cells are cultured inside the lumen of fibers, and the medium flows in the shell of fiber (Fig. 1) (Nyberg et al. 1994). More complex devices have been explored for the culture of hepatocytes, stem cells, and progenitor cells that include the use of different fibers. A bioreactor with four interwoven independent capillary membrane systems that serve different functions has been developed by Gerlach et al. (1994). The cells are cultured on the outer surface and among the capillaries. Each fiber type exhibits a different function: silastic membranes for oxygen supply and removal of carbon dioxide, polyamide fiber for the plasma inflow, polyethersulfone fiber for the plasma outflow, and hydrophilic polypropylene

membranes for the sinusoidal endothelial coculture. A crossed hollow fiber membrane bioreactor was developed as an *in vitro* liver tissue model to study disease, drugs, and therapeutic molecules alternative to animal experimentation (De Bartolo et al. 2009). The bioreactor consists of two types of fibers with different MWCO and physicochemical properties cross-assembled in alternating manner: modified polyether-etherketone and polyethersulfone used for the medium inflow and outflow, respectively. The combination of these two fiber sets produces an extracapillary network for the adhesion of cells and a high mass exchange through the crossflow of culture medium. This bioreactor has been developed for the culture of human hepatocytes and expansion and differentiation of liver progenitor cells. Multibore fiber membrane bioreactor consisting of modified polyethersulfone fiber has been developed for the long-term maintenance of human hepatocytes. Each fiber is composed of seven compartments that communicate through a porous foamy support structure that is located in between the capillaries. Cells have been cultured inside the lumen of the multibore fibers and lumen in the shell compartment (De Bartolo et al. 2007b).

Hollow fiber membrane bioreactors have a great potential for the expansion and differentiation of embryonic and adult stem cells, which have ability to either self-renew or differentiate into multiple cell lineages. These properties make stem cells attractive as a cell source for cell therapies, tissue engineering, and model systems for drug screening. Depending on the application, hollow fiber membrane bioreactors can be used for the production of expanded stem cells with uniform properties and/or for a controlled and reproducible differentiation into selected mature cell types (Salerno et al. 2013). They are particularly advantageous with respect to the other culture systems because of their capacity to ensure a more homogeneous environment, to monitor key culture parameters (pH, temperature, oxygen, etc.), and to guide the transdifferentiation of cells by engineering membranes with targeted properties.

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Hollow Fiber Membrane Module

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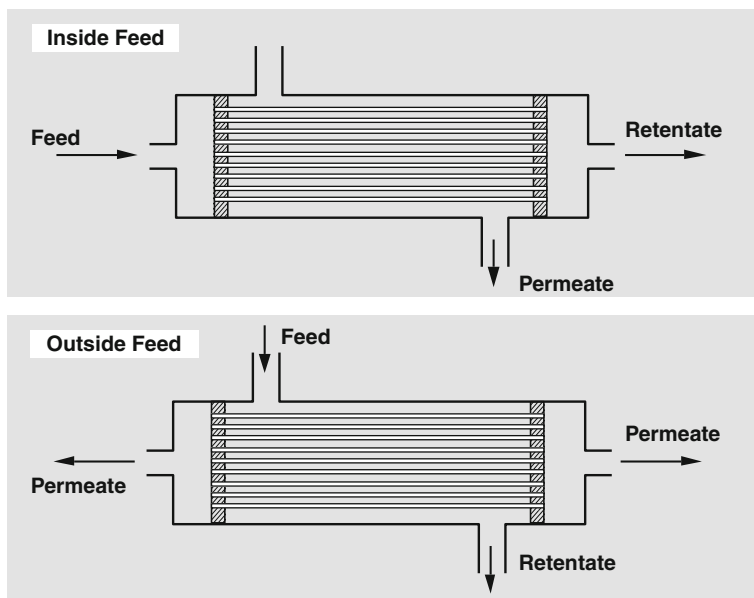
Synonyms

[Hollow fiber membrane](#); [Hollow fiber module](#)

The hollow fiber membrane module as well as a capillary membrane module assembles as shell-and-tube heat exchanger. It consists of a large number of hollow fibers assembled in a module,

Hollow Fiber Membrane Module, Fig. 1

Schematic of a hollow fiber module with the feed on the inside of the fiber (bore side feed) and the feed on the outside of the fibers (shell side feed) (Taken from Scholz et al., 2011)



as shown schematically in Fig. 1 (Scholz et al. 2011; Mulder 1997).

The free ends of the fibers are potted with agents such as epoxy resins, polyurethanes, silicone rubber, thermoplastics, thermosets, or inorganic cements. In some cases, they can also be fused by heating. The difference between hollow fiber modules and capillary modules is a matter of dimensions while the module concepts are the same (Scholz et al. 2011; Mulder 1997).

Hollow fibers consist of a porous, nonselective support layer (about 200 μm) and an active layer (<40 nm). The active layer is the actual membrane, but due to its small thickness, it must be supported by a thicker layer in order to obtain mechanical strength, to withstand the pressure difference between feed to permeate side (Scholz et al. 2011).

The hollow fiber membranes are self-supporting. Two types of module arrangement can be distinguished: (i) where the feed passes through the bore of the hollow fiber (lumen) whereas the permeate is collected on the outside of the hollow fibers (Fig. 1 “Inside Feed”) and (ii) where the feed enters the module on the shell side of the hollow fibers (external) and the permeate passes into the fiber bore (Fig. 1 “Outside Feed”). The choice between the two concepts is mainly

Hollow Fiber Membrane Module, Table 1 Properties of hollow fiber modules (Taken from Scholz et al. 2011)

	Hollow fiber module
Structure	Self-supporting
Active layer	Inner/outer diameter
Feed	Lumen/shell side
Inner diameter	40–250 μm
Outer diameter	80–400 μm
Packing density	<10,000 m^2/m^3
Allowed pressure	100 bar shell side; 15 bar lumen side
Applications	GP, RO, DL

based on the application where parameters such as pressure, pressure drop, type of membrane available, etc. are important. Depending on the concept chosen, asymmetric hollow fibers are used with their skin on the inside or on the outside (Mulder 1997).

The hollow fiber module is the configuration with the highest packing density, which can attain values of 30,000 m^2/m^3 (Scholz et al. 2011). The typical properties and dimensions of hollow fiber membrane modules are summarized in Table 1 (Melin and Rautenbach 2007):

The advantages of hollow fiber modules are the following (Melin and Rautenbach 2007):

- Highest packing density and membrane area to module volume ratio
- Cheapest manufacturing costs

The disadvantages are the following:

- Mostly laminar flows (increased mass transfer limitations)
- Lower pressure resistance

Up to 80 % of the commercial gas separation membranes are being formed into hollow fiber modules (Baker 2002).

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Hollow Fiber Module

► Hollow Fiber Membrane Module

Hollow Fiber Modules for Desalination

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The desalination of brine is commercially implemented by reverse osmosis (RO),

multi-effect evaporation (MED), and multistage flash (MSF) distillation. Although such conventional processes are widely used, there is a need for novel desalination techniques such as membrane distillation (MD) which may be much cheaper and have other distinct advantages. The membranes used in MD processes can be divided into two forms: flat sheet membrane and hollow fiber-based membrane. Most of the work on hydrodynamic improvement in MD studies has focused on flat sheet membrane modules. They have small membrane areas and thus are limited to laboratory research. In industry, hollow fiber-based membrane modules are preferable due to their larger membrane area per unit volume and reduced vulnerability to temperature polarization. Based on the MD mechanism, the obtained flux depends both on the membrane permeation properties and the flow geometry in the membrane modules. Therefore, the research on the flux enhancement in MD can be divided into two large areas, the fabrication of highly permeable membranes and designs of optimized membrane modules.

Recently, many designs of hollow fiber membrane modules have been proposed in order to suppress the undesirable temperature and concentration polarization phenomena. The performances of different polyvinylidene fluoride (PVDF) hollow fiber membranes have been studied in different size modules (Fig. 1). The properties of the laboratory modules made, which depend on the experiment's requirements, can be changed. The modules of PVDF have a stable performance and can be used in reverse osmosis drained wastewater treatment (Wu Chunrui et al. 2010). The study in comparison of three membrane distillation configurations and seawater desalination by vacuum membrane distillation (VMD) showed that the shell-and-tube capillary membrane module had unique advantages such as flexible and changeable (Chen Huayan et al. 2011).

Li et al. designed a novel membrane device made of novel membranes. To enhance the brine side heat transfer coefficient substantially, they employed cross flow of hot brine over the outside surface of hollow fiber membranes. To achieve a compact device, they designed a hollow fiber

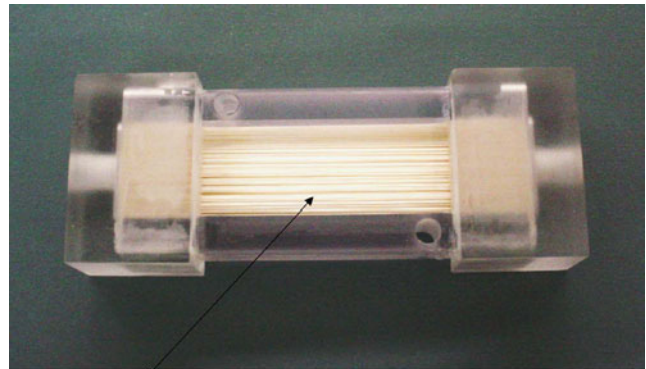
Hollow Fiber Modules for Desalination,

Fig. 1 Modules of PVDF hollow fiber membrane



Hollow Fiber Modules for Desalination,

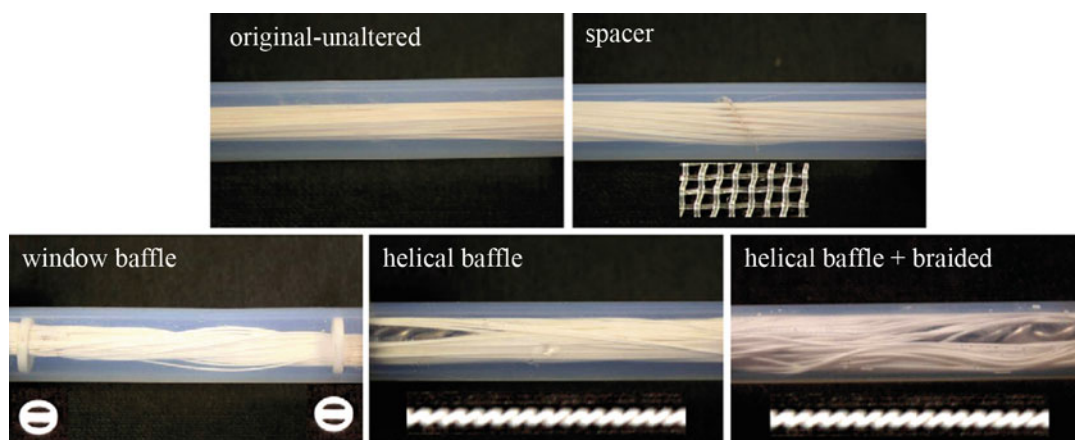
Fig. 2 Rectangular cross flow test module without face plates



Hollow fibers

device built in a rectangular cross flow mode for the hot brine to flow over the outside of the fibers (Fig. 2) (Li and Sirkar 2005). Simplified models have been developed to describe the observed performance of the modules in different MD

processes (Gilron et al. 2007). The MD experiment's results have shown that the modules' performance was quite satisfactory and the design of module enhanced the heat transfer as well as mass transfer.



Hollow Fiber Modules for Desalination, Fig. 3 Different modules design and hollow fiber geometries configurations

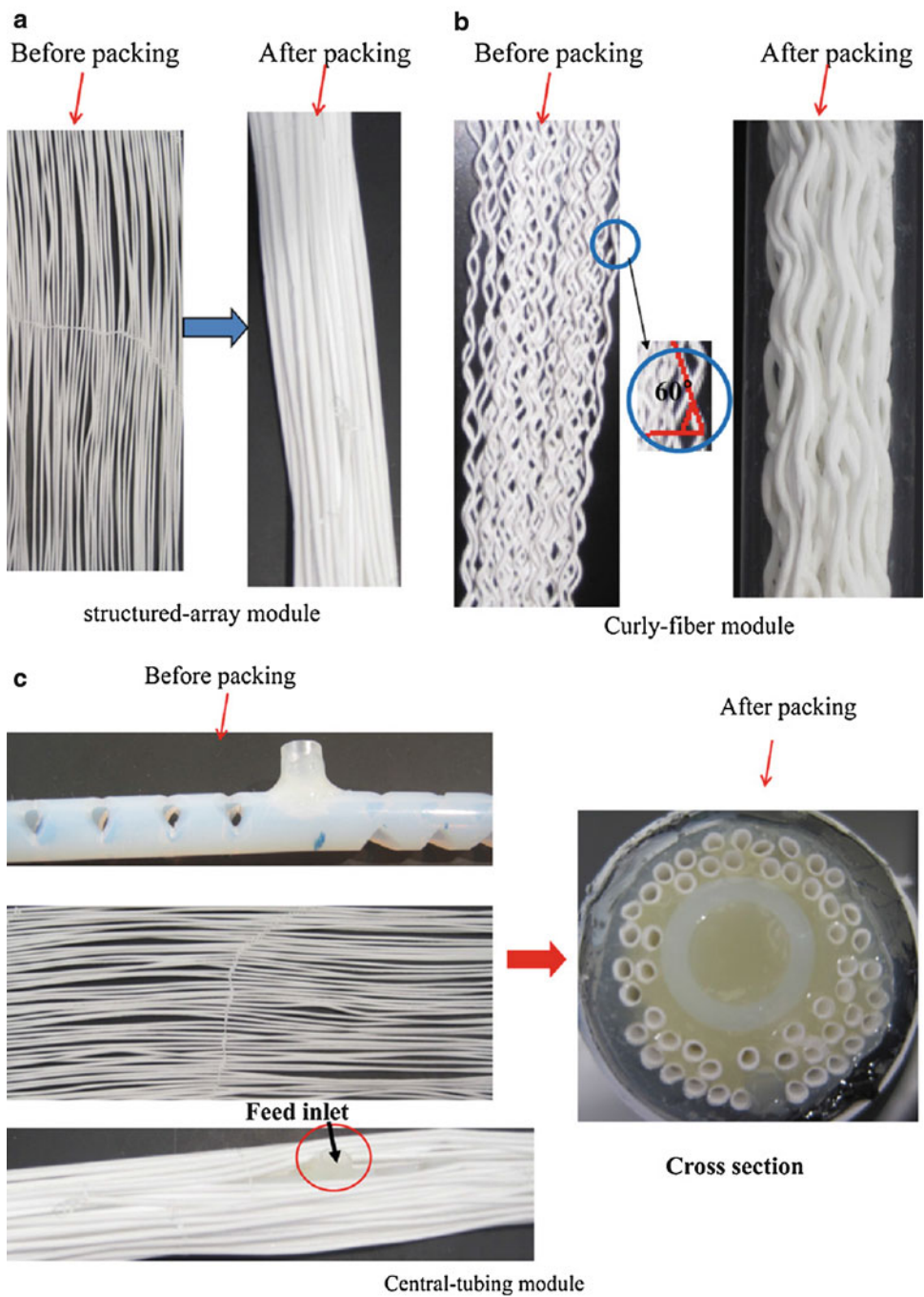
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Different hollow fiber configurations with wavy geometries (twisted and braided) for flux enhancement in MD process have been developed by Teoh et al. in 2008 (Teoh et al. 2008). The different module designs, such as baffles and spacers, were incorporated during the module fabrication process, as illustrated in Fig. 3. A single sieve spacer was placed about 7.5 cm away from both ends of the module in the spacer module designs. And the distance between each spacer for the two or three-sieve spacers configurations was 5 or 3.75 cm. Similarly, the helical baffle introduced in the central of the module which was surrounded by hollow fibers was placed 5 cm away from the both ends of the membrane module. The results showed that the application of baffles can increase the feed side heat transfer coefficient. In addition, using spacers among the fibers may increase the effective membrane area 18–33 %. Lastly, the application of different hollow fiber configurations with wavy geometries could lead to flux enhancements as high as 36 % without inserting any external turbulent promoter. In overall, the goal of greater flux enhancements with modified hollow fiber membranes modules was achieved.

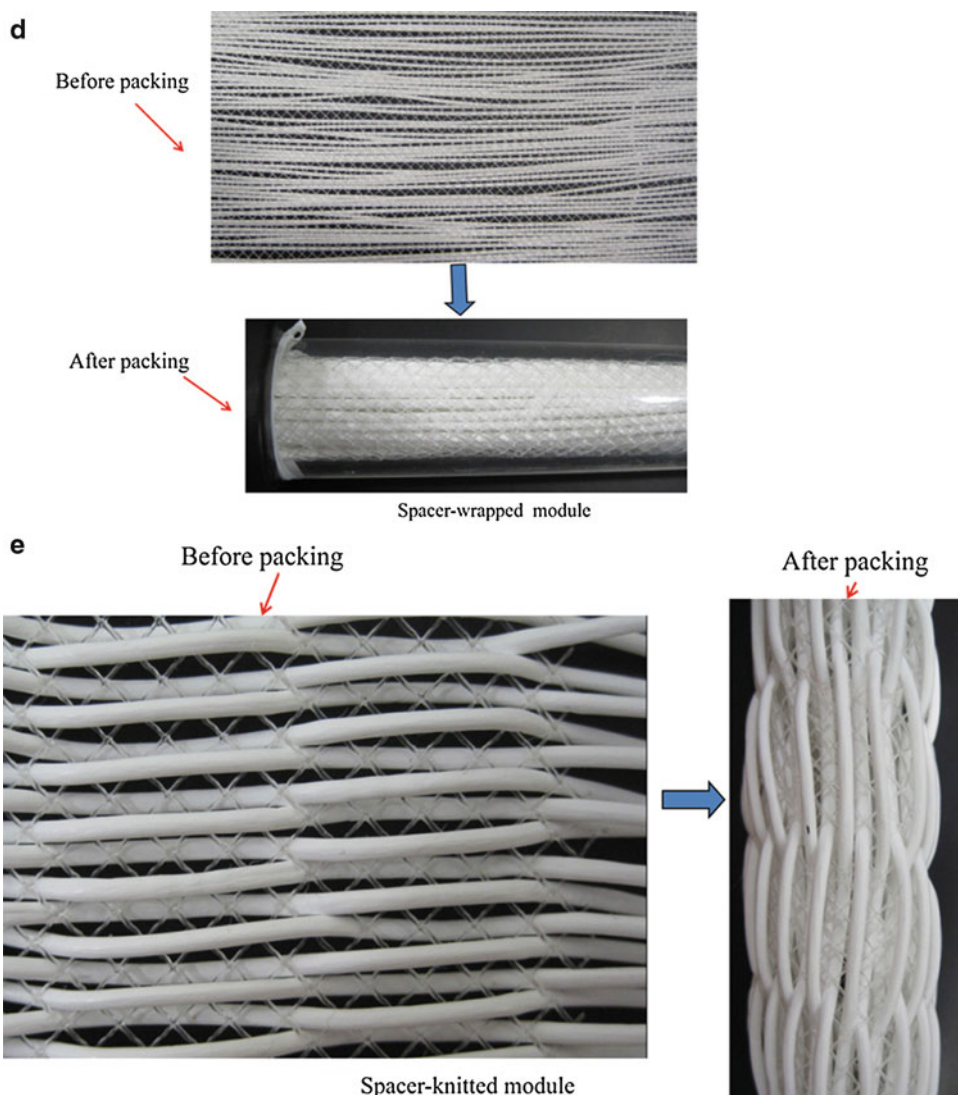
Five types of novel hollow fiber module configurations have been designed and constructed by Yang et al. for the direct contact membrane distillation (DCMD) process in 2011

(Yanga et al. 2011). The novel designs could be divided into structured-straight fibers, curly fibers, central tubing for feeding, spacer-wrapped fibers, and spacer-knitted fibers. The test results showed that the vapor permeate flux could be enhanced from 53 % to 92 % compared with the conventional module, and the spacer-knitted module had the best performance. Experiments reveal that improved fiber geometries or arrangements can provide a better flow distribution, thus much lower pumping energy cost and higher thermal efficiency could be accomplished (Fig. 4).

In 2005, Liu et al. prepared some coiled hollow fiber membrane modules and experimentally examined their mass transfer performances (Liu et al. 2005). The research results showed that, compared with the conventional straight module, the mass transfer in both tube and shell side of the coiled hollow fiber module could be remarkably enhanced. And the mass transfer coefficient of the coiled module at either side of membrane was more than two times higher than that of the straight module. The configurations of the coiled hollow fiber membrane module and the conventional straight module are shown in Fig. 5. Different geometric coiled modules were employed to study the influences of the factors such as coiled diameter, wind angle, and internal diameter of fibers on mass transfer. It was found that wind angle had an



Hollow Fiber Modules for Desalination, Fig. 4 (continued)



H

Hollow Fiber Modules for Desalination, Fig. 4 Novel module design and fabrication: (a) structured-straight module; (b) curly-fiber module; (c) central-tubing module; (d) spacer-wrapped module; e spacer-knitted module

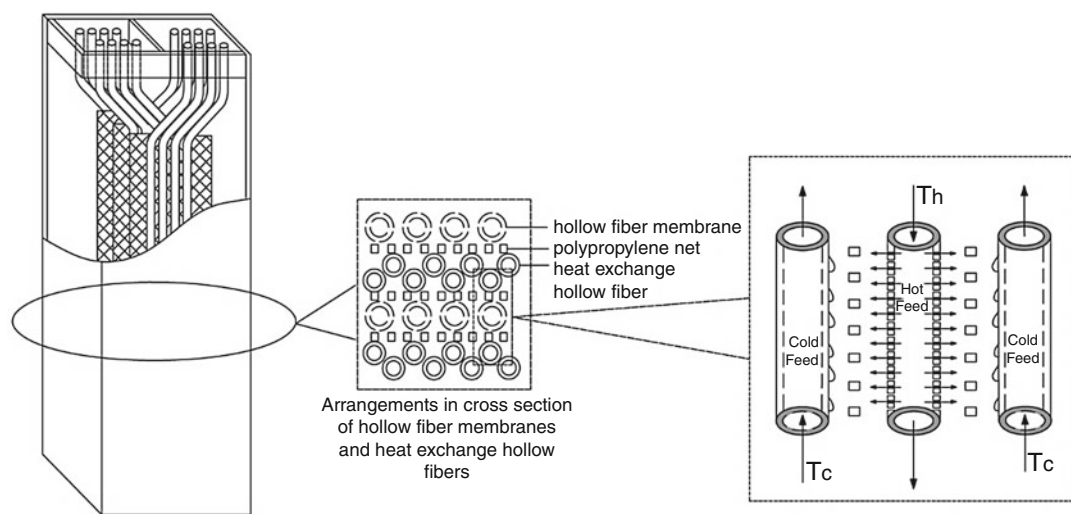
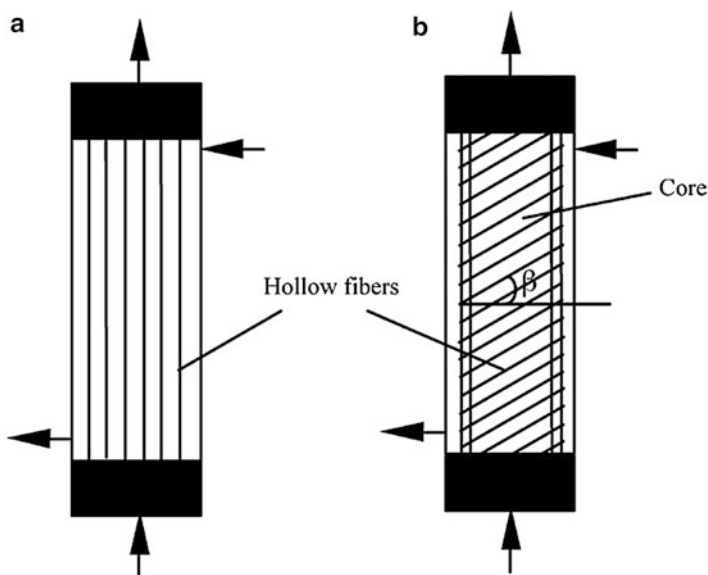
important influence on the fluid condition of the coiled module and its mass transfer.

Geng et al. developed a new air-gap membrane distillation (AGMD) module with internal latent heat recovery configuration (Geng et al. 2014). The novel module is consisted of parallel hollow

fiber membranes and heat exchanged hollow fibers (Fig. 6). They investigated the influences of operating factors such as feed flow rate, feed temperature, and feed initial concentration on AGMD process. Simultaneously they established a theoretical model based on the energy and mass

Hollow Fiber Modules for Desalination,

Fig. 5 Schematic representation of straight module (a) and coiled module (b)



Hollow Fiber Modules for Desalination, Fig. 6 Schematic presentation of the novel AGMD module

balances of the hot feed side in membrane. The model was used to calculate the temperature and the vapor permeate flux distributions along the hollow fiber membrane. The performance of the AGMD module was experimentally demonstrated under different operating conditions, and the results showed that the energy of AGMD process was recycled effectively, simultaneously, a high gained output ratio (GOR) of 5.7 was obtained.

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Hollow Fiber Spinning

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Hollow fibers are fabricated by extruding or pumping a dope solution through a spinneret following different methods such as melt spinning, dry spinning, wet spinning, or dry/wet spinning. The spinneret has a tube-in-orifice structure with typical dimensions 0.5–1 mm inner diameter and 0.9–2 mm outer diameter. A simple experimental device for the hollow fiber spinning by dry/wet spinning is shown in Fig. 1. In some spinning systems, a circulation pump is employed instead of the gas cylinder (i.e., nitrogen) to drive the dope solution through the spinneret. The dope solution under gas pressure is forced to pass through the spinneret the annular space of the spinneret. The internal coagulant (bore liquid) is driven through the central tube either by the gravity force or by means of a circulation pump. The dope solution, after being extruded from the spinneret, enters into a coagulation bath before traveling a certain distance of air gap (i.e., the distance between the spinneret and the coagulation bath), which may

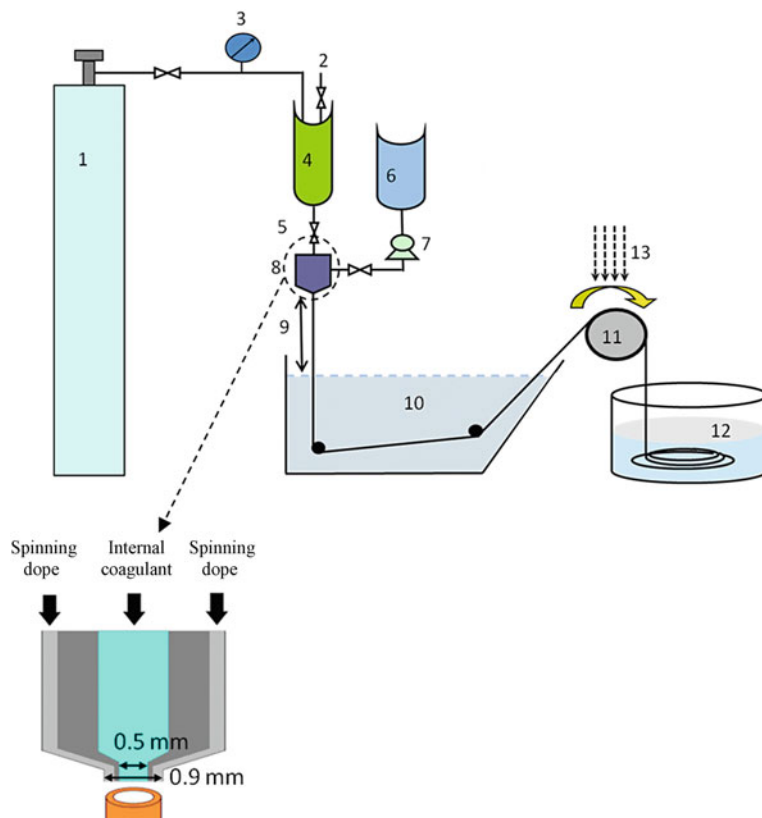
vary from 0 (wet spinning) to more than 1 m. In wet spinning, the dope solution is extruded directly into the precipitating liquid (external coagulant). In this technique the spinneret is submerged in the coagulation bath causing immediate fiber precipitation and solidification. In the dry/wet spinning, coagulation of the internal surface of the nascent fiber starts immediately after its extrusion from the spinneret, whereas the external surface experiences coalescence and orientation of polymer aggregates through the air gap before gelation in the external coagulation bath takes place. After spinning, the nascent fibers are oriented by means of guiding wheels and finally pulled into a collecting reservoir by a wind-up drum. Only a fiber with sufficient mechanical integrity can pass over the guiding wheels to the collecting bath. During spinning, the take-up velocity is generally kept at the same speed as the free-falling velocity of the nascent fiber to prevent stretching of the fiber (Khayet and Matsuura 2011).

Prior to the drying step, the spun hollow fibers usually go through the solvent exchange and other posttreatment procedures in order to remove residual solvents, prevent hollow fiber shrinkage, eliminate possible defects, and reduce pore collapse. Conventional solvent exchange step before drying consists of immersion of the obtained hollow fibers in one non-solvent or successive immersion in several non-solvent mixtures containing components with lower surface tensions than water. Mixtures of water with increased concentrations of lower surface tension components such as methanol and ethanol can be employed. Hexane can also be employed for further solvent exchange since its surface tension is even lower than alcohols and it is volatile.

The hollow fibers can be spun at room temperature (20–22 °C) or at a temperature higher than the ambient temperature. During spinning the take-up speed is normally maintained nearly the same as the dope extrusion speed so that no external elongational stresses, except gravity, can be applied to the nascent hollow fiber. A very large air gap distance may lead to flow instability of the fiber resulting in nonuniform fiber dimensions. Examples of typical applied spinning parameters

Hollow Fiber Spinning,

Fig. 1 Schematic diagram of a typical hollow fiber spinning system: 1 spinning dope tank; 2 regulating pressure valve; 3 pressure gauge; 4 dope vessel; 5 dope valve; 6 bore liquid vessel; 7 bore liquid pump; 8 spinneret; 9 air gap; 10 coagulation bath; 11 wind-up drum; 12 fiber collecting reservoir; 13 wash water (Reprinted from Khayet et al. (2009). Copyright 2009, with kind permission from Elsevier)



of different poly(vinylidene fluoride), PVDF, dope solutions are bore liquid flow rate (0.5–3 ml/min), air gap distance (0–3 cm), take-up speed (free fall, 5 m/min), dope solution flow rate (2–4 ml/min), applied pressure over the dope solution (138–207 kPa), and temperature of the coagulants (15.5–25 °C) (Wu et al. 2005, 2006, 2007; Wang et al. 2008).

In dry spinning, air or an inert gas is used instead of the bore liquid so that solidification is achieved through evaporation of the solvent. As the dope solution exit the spinneret, air or an inert gas is used to evaporate the solvent(s) so that the fiber solidifies and collected on a take-up wheel. Spinning is followed by stretching of the as-spun fibers to orient the polymer chains along the gas gap (i.e., fiber axis). The as-spun fibers do not come into contact with a precipitating liquid. In dry spinning and melt spinning, the dimensions of the spinneret are not so crucial because the fiber dimensions are mainly determined by the ratio of the extrusion rate and “tearing rate” (Mulder 1992). The gas flow

used for solvent evaporation and solidification of the fibers influences to a significant extent the quality of the produced fibers.

In melt spinning, the polymer is first compressed, heated, and melted by an extrusion screw, then forced through the annular space of the spinneret. The polymer solidifies by cooling after being extruded from the spinneret and then collected by means of take-up wheels. The spinning rate in melt spinning (thousands of meter per minute) is much higher than that used in the dry/wet spinning technique (meters per minute) (Mulder 1992).

The spinneret geometry, the dope solution, and the spinning conditions (bore fluid type and its flow rate, dope solution extrusion rate, take-up speed, air gap distance, external coagulant, spin draw ratio, spinning temperature, cold stretching, etc.) affect the hollow fiber geometrical parameters (inner and outer diameters, thickness), its internal structure, as well as the structural morphology of the inner and outer surfaces.

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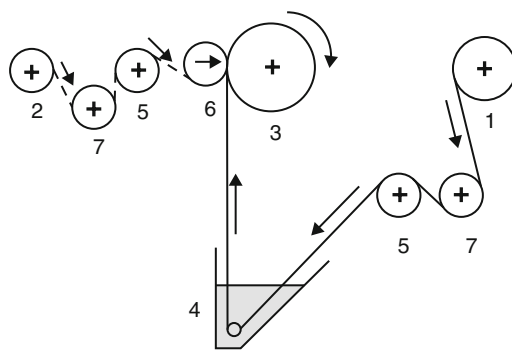
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Homogeneous Anion-Exchange Membranes

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Anion-exchange membranes (AEMs) are classified into two types by their microstructure: heterogeneous and homogeneous. Homogeneous AEMs consist of a uniform membrane matrix with anion-exchange groups (positively charged groups) and, in many cases, reinforcing materials such as woven cloth or net. Various methods have been reported for preparing homogeneous AEMs; however, almost commercial homogeneous AEMs are copolymer membranes composed of styrene and divinylbenzene (DVB) with benzyl trimethylammonium groups. Figure 1 shows a schematic diagram of a typical preparation method (paste method) of the AEMs



Homogeneous Anion-Exchange Membranes, Fig. 1 A typical preparation method of AEMs (paste method). 1 Reserve roll of reinforcing fabric, 2 reserve roll of separating film, 3 receiving roll, 4 paste (mixture of vinyl monomers, inert polymers, initiator, additives, etc.) reservoir, 5 expand roll, 6 press roll, 7 guide roll

(Sata 2004). A monomer mixture consisting of chloromethylstyrene (CMS)/DVB, acrylonitrile-butadiene rubber, and benzoyl peroxide to initiate polymerization was used to prepare the paste. A reinforcing material such as woven poly (vinyl chloride) cloth, reserved to roll 1, was dipped in the paste reservoir 4. A separating film such as poly(ethylene terephthalate) was fed from roll 2. The reinforcing material coated with the paste was wound on roll 3 in layers with the separating film. In this way, the paste (the monomer mixture) was continuously coated on the reinforcing material and covered on both sides with the separating film. A precursor membrane was obtained by heating the resultant composite at 80 °C for 10 h under a nitrogen atmosphere to polymerize the monomers. An ion-exchange group was introduced by quaternization by immersing the precursor membrane in an aqueous solution of 1.0 mol/dm³ trimethylamine at 30 °C for 20 h. The cross-linker content (CLC) in the mixture was changed to control the network structure of the membranes. The CLC was defined as follows:

$$CLC = \left(\frac{C_{DVB}}{C_{CMS} + C_{DVB}} \right) \quad (1)$$

where C_{DVB} and C_{CMS} are the content of DVB and CMS in the mixture. The value of CLC is controlled to optimize the fundamental

physicochemical properties, transport number of anions and electrical resistance, to their applications. In general, the transport number and electrical resistance of AEMs increase with increasing *CLC*.

Other preparation methods of homogeneous AEMs have been reported such as: (a) modification of aromatic polymer. An aromatic polymer such as poly(ether-ether-ketone) is chloromethylated using chloromethyl ether in the presence of a catalyst, and then the chloromethylated polymer is quaternized using triethylamine. The quaternized polymer solution is cast to form an AEM. (b) Pore-filling method. AEMs are prepared by filling the pores of a porous film (e.g., porous polyethylene) with a mixture of vinylbenzene-based monomers, a cross-linking agent, and an initiator. Then, thermal cross-linking polymerization is performed. Finally, quaternary ammonium groups are introduced. (c) Electron-beam-induced graft polymerization. A polymer film such as high-density polyethylene is grafted by electron-beam-induced graft polymerization with CMS and DVB. The quaternary ammonium groups are introduced by treating the grafted film with trimethylamine.

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Honeycomb Ceramic Membranes

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Honeycomb structure body possesses a specified pore distribution on the surface of the partition walls and an enlarged porosity in addition to thin partition walls of a prescribed value. Because of the special structure, ceramic honeycombs are

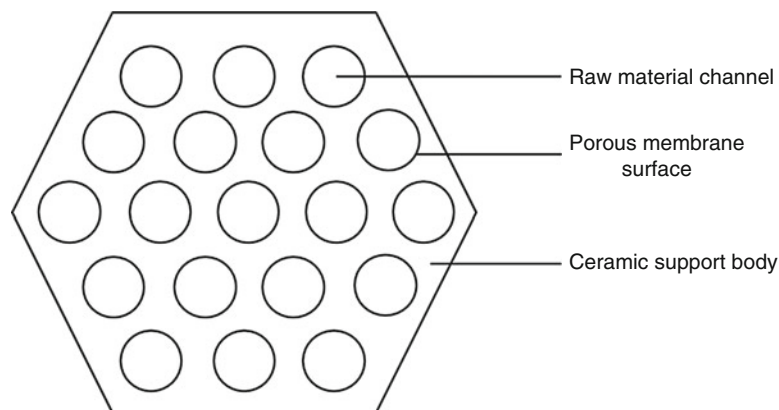
widely used as catalyst supports and as particulate filter (Pronob 1997).

The honeycomb membrane is viewed as a type of multichannel membranes. It brings the element of ceramic honeycomb monoliths, with proprietary modifications, as membrane supports. Such large honeycomb structures are characterized by very high membrane area, up to several hundred-fold the amount of area in most commercially available ceramic membrane elements. Variations such as adding the pore numbers and decreasing the diameter of every pore will improve membrane area. The loading density of ceramic membrane is also improved with the honeycomb design. The cross section schematic diagram of honeycomb ceramic membrane is shown in Fig. 1.

However, there are disadvantages in honeycomb ceramic membrane. The first disadvantage is asymmetry distribution of fluid. Because of the honeycomb element of high sectional area, the volume of membrane is relatively large. It will lead to the consequence that the velocity of fluid in honeycomb ceramic membrane which is coaxial to pipe of raw materials is higher than fluids from other fluids. So it is hard to control concentration polarization in membrane as the asymmetry distribution of fluid. Another disadvantage is high permeate pressure. With decrease of pore diameter and pore wall thickness, more permeate liquid passes through inner pore of honeycomb ceramic support. So the transmission resistance is improved, permeation flux is decreased. Using the method to change parts of membrane pores to permeation flux channel, or to slot ports, permeation length is decreased and permeation flux is improved. But unit area of membrane decreases in some extent. So post-processing of honeycomb ceramic membrane is extremely important, despite of its difficulties. The other disadvantage is high cost with low yield. Since the preparation process is very complex, probabilities of membrane defects are much higher. Those defects can be improved with designed membrane modules.

The use of honeycomb structure in ceramic membrane is promising. It has been used in reverse osmosis desalination for sea water. Exploratory and advanced developments have been accomplished in some companies. With

Honeycomb Ceramic Membranes, Fig. 1 The cross section schematic diagram of honeycomb ceramic membrane



mean pore size of 50 nm, honeycomb ceramic membrane improves the quality of pure water in osmosis process to 86 %. And the permeation flux can be kept in about 150 L/(m²·h·bar) according to experiments mentioned in several articles.

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Honeycomb Membrane

► Monolithic Membranes

Honeycomb Membrane Structure

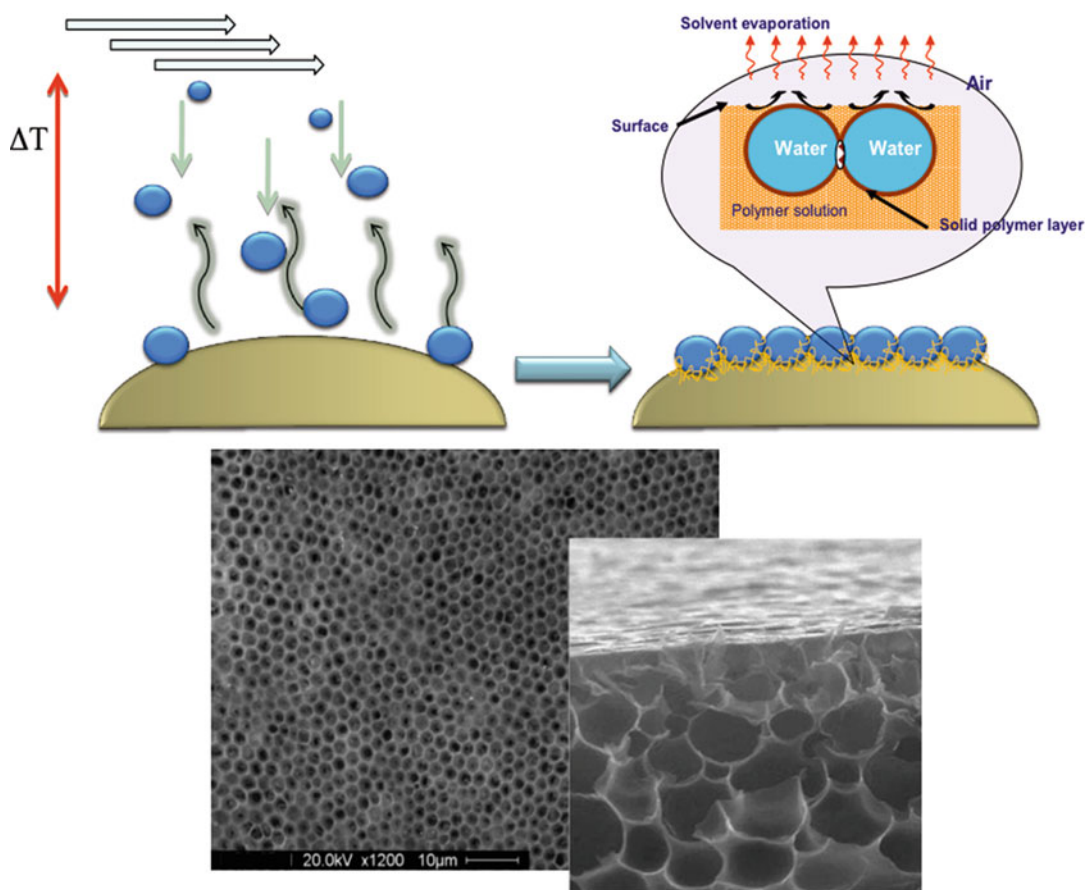
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Synonyms

Air bubble geometry; Breath figure membranes; High-defined porous films

Honeycomb membrane structures are a competitive and concrete example of highly ordered polymeric patterns, which can work as perm-selective interfaces in advanced membrane processes (Gugliuzza et al. 2008). They are prepared by using a bioinspired nanotechnology, which exploits the ability of water to condense from fog to cooled surfaces and self-assemble in semi-crystalline lattices under dragging Marangoni convection and capillary forces (Gugliuzza et al. 2009). When the solvent evaporates, a difference of temperature is established between the cooled liquid film and nearby humid atmosphere, causing droplets to condense and rearrange in honeycomb-packed geometries. The droplet lattice works as a real pore builder through the polymeric solution, leading to the formation of air bubble arrays. Each single cavity can be regarded as the result of the imprinting action of the droplets. No coalescence is observed when a stable polymeric protective layer is formed around each single droplet during sinking (Fig. 1).

Under suitable experimental conditions, droplet dynamics can be directed towards the formation of membranes with modulated spherical pore size, monodisperse pore distribution, long-range order, and high interconnectivity (Speranza et al. 2010). The typical hexagonally packed geometry, resembling natural structures, produces very high interfacial area necessary to promote large mass transfer through the membranes. Also, the complete propagation of the porous structure along the entire membrane thickness reduces significantly any resistance to transport,



Honeycomb Membrane Structure, Fig. 1 Representative mechanism for the formation of honeycomb membranes

yielding performance higher than that observed for commercial tubular modules when worked in membrane distillation plants (Gugliuzza et al. 2008).

The singular topography of honeycomb membranes has significant consequences on wettability as well. The hexagonally packed geometry increases the surface roughness according to zig-zag geometrical model (Thomas 1999), preventing wetted pores owing to air pockets uniformly distributed through the surface. Indeed, the air is easily entrapped inside the big cavities according to the Cassie–Baxter model, thereby minimizing the spreading of the liquid and improving significantly the water resistance of the membrane.

Chemical and structural features make the honeycomb membranes ideal interfaces for some membrane contactors operations, including membrane distillation, membrane crystallization, and membrane emulsification (in particular premix membrane emulsification), where large mass transfer along with the establishment of durable interfaces at the entrance of each single pore are in great demand. Moreover, the extraordinary regularity and stability of 3D polymeric architecture make these membranes suitable for working as molecular reservoirs, scaffolds for tissue engineering, and platforms for sensors.

Compared with traditional manufacturing procedures, the one-pot fabrication of micro- and nanostructured membranes, based on the self-

assembly of sacrificial natural building blocks, is regarded as a novel, flexible, and eco-friendly technology. This approach is expected to open new routes to fabricate a large variety of ordered functional membranes for industrial applications, but also for handling the miniaturization of light-weight systems perceptively.

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Horizontally Aligned Carbon Nanotube

► Aligned Carbon Nanotube

Hybrid Membranes

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The term “hybrid membrane” more commonly refers to a membrane formed by at least two components of different chemical nature (considering chemical-bond modes) from the groups of metals, organic materials and their polymers, and inorganic materials.

Hybrid membranes can be classified into two main types, depending on the nature of the interaction between components: (1) systems where there are no covalent or ionic-covalent bonds between components, only Van der Waals, hydrogen bonding, or electrostatic forces, and (2) systems where at least parts of the components are linked through strong covalent or ionic-covalent bonds (Sanchez and Gómez-Romero 2004). The first type can also be named as composites, or nanocomposites, where at least one of the components' domains has a dimension ranging from a few angstroms to several nanometers.

The main objective in the synthesis of hybrid membranes is the performance improvement of the material for different applications. It is obvious that the properties of these membranes are not only the sum of the individual contributions of both components, and interfaces can play a significant role.

The high number of parameters involves in the design and preparation of hybrid membranes: the number of components, composition, components ratio, size, shape, and kind of interaction between components results in an almost infinite number of combinations.

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Hybrid Modeling of Membrane Biofilm Reactors

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The immobilized whole cells in a membrane bio-reactor are grown within the fibers and/or in the

extracapillary space-forming biofilm. The conventional biofilm is increasingly used for wastewater purification, oxidation of organic components, nitrification, etc. as they are environmentally friendly and less energy intensive. Biofilm formation is a complicated dynamical process governed by various physical and chemical principles and biological protocols. Biofilms are agglomerations of microorganisms or bacteria whose structure can be homogeneous, in case of sufficient substrate level, or heterogeneous when the diffusion is rate limiting, due to the change of the nutrient concentration in axial direction (Gavin and Gillian 2012). This circumstance can alter the value of transport parameters (diffusion coefficient, convective velocity) and can even alter the biochemical reaction rate (the consumption rate of nutrient). The variation of cell density is also true in the biocatalyst membrane layer perpendicular to the inlet surface. Increasing distance from the surface can mean decreasing nutrient concentration. That is why the variability of the transport parameters should also be taken into account. Assuming simultaneous effect of two substrates, namely, oxygen and carbon sources, the mass balance for diffusive flow can be given for a sheet membrane layer with constant parameters, as

$$D \frac{d^2 c_{O_2}}{dy^2} - \frac{1}{Y_{XO_2}} \frac{\mu_{\max O_2} c_{O_2}}{K_{MO_2} + c_{O_2}} \frac{c_A}{K_{MA} + c_A} = 0. \quad (1)$$

The quasi-analytical approach of solution of Eq. 1 is given, e.g., by Nagy (2011). Let us give here the rate equations for limiting cases with constant c_A concentration in the biofilm. Two important cases can be distinguished, namely, when the outlet (at $y = \delta$) diffusive flow is zero ($dc/dy = 0$, the support membrane layer is impermeable) and $dc/dy \neq 0$ at $y = \delta$ (there is sweep phase on the permeate side of a permeable membrane). The mass transfer rates are given for these cases, for first-order reaction by Eqs. 2 and 4 and for zero-order reaction by Eqs. 5 and 7, respectively. The transfer rate in the presence of convective flows is given in entry biocatalytic membrane

reactor: mass transport ($c = c_{O_2}$, Y_{XO} is yield coefficient):

$$J = \sqrt{k_1 D} \tanh \vartheta c^o \quad (2)$$

with

$$\vartheta = \sqrt{\frac{k_1 \delta^2}{D}}; \quad k_1 = \frac{1}{Y_{XO}} \frac{v_{\max}}{k_{MO_2}}$$

$$J = \frac{\sqrt{k_1 D}}{\tanh \vartheta} \left(c^o - \frac{c_\delta}{\cosh \vartheta} \right) \quad (3)$$

$$J = \frac{D}{\delta} \vartheta^2 c^o \quad (4)$$

with

$$\vartheta = \sqrt{\frac{v_{\max} \delta^2}{D Y_{XO_2}}}$$

$$J = \frac{D}{\delta} \left(c^o - c_\delta - \frac{\vartheta^2}{2} \right) \quad (5)$$

In order to overcome the diffusive mass transport limitation of nutrients, especially of the sparingly soluble oxygen, the substrate might be fed on both sides of the biofilm applying oxygen permeable support layer. The sum of the mass transfer rates for first- and zero-order reactions can be expressed by Eqs. 6 and 7, respectively. The substrate concentrations of the two sides of the biofilm layer are c_1^o and c_2^o . The substrate concentration curve has inflection point at $Y = Y_1$ ($Y = y/\delta$):

$$J = \frac{\sqrt{k_1 D}}{\tanh \vartheta} \left\{ \left(1 - \frac{1}{\cosh^2(\vartheta Y_1)} \right) c_1^o + \left(1 - \frac{1}{\cosh^2(\vartheta [1 - Y_1])} \right) c_2^o \right\} \quad (6)$$

with

$$\frac{c_1^o}{c_2^o} = \frac{\cosh(\vartheta Y_1)}{\cosh(\vartheta [1 - Y_1])}$$

$$J = \frac{D}{\delta} \left\{ c_1^o + c_2^o - 2c_1^o \left(1 - \frac{\vartheta^2}{2} [2Y_1 - 1] \right) + \vartheta^2 \right\} \quad (7)$$

with

$$\begin{aligned} c_1^o \left(1 - \frac{\vartheta^2}{2} [2Y_1 - 1] \right) \\ = c_2^o \left(1 + \frac{\vartheta^2}{2} [2Y_1 - 1] \right). \end{aligned} \quad (8)$$

The Y_1 inflection point can be determined by Eq. 8 and then the mass transfer rate by Eq. 7 as well. Detailed solution of Eq. 1 is published by Nagy (2011), recommended explicit expression for the mass transfer rate. The biofilm can involve several substrates with several parallel and/or consecutive reactions as this is the case of aerobic wastewater treatment. System of the differential mass balance equations of the reactants should be solved in order to get their concentration distributions and the mass transfer rates of the transferring substrates.

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Hybrid Organic-Inorganic Nanostructured Membranes

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A hybrid organic-inorganic nanostructured membrane is a specific kind of hybrid membrane formed by at least two components from organic materials and their polymers and inorganic materials. The components of this kind of hybrid membranes have dimensions up to several nanometers, and components are linked through covalent or ionic-covalent bonds.

Improved and also new properties are expected in this specific kind of hybrid membranes because of the combination of two very different materials and their chemical interactions. For example, it is possible to obtain membranes with a high flexibility and processability, such as a polymer, but with the improved thermal and chemical stability, and mechanical strength of inorganic materials (Sanchez et al. 2005).

The possible applications of these hybrid membranes are increasing continuously. For example, an antimicrobial drug (substituted 1,3,4-oxadiazole) with functionalized silica was successfully incorporated into an organic phase by sol-gel to achieve a highly stable and anti-biofouling membrane for water treatment (Singh et al. 2012). Hybrid organic-inorganic nanostructured membranes have also found applications in the medical field for advanced separation of heavy metals from blood or other physiological liquids, such as new polymeric-carbon nanotube composite membranes based on polysulfone with different types of nanotubes (Nechifor et al. 2009). Another important area where these hybrid membranes may have a significant relevance is the energy sector, especially as new membranes for proton exchange membrane fuel cells (PEMFC) and solid-state Li-ion batteries. These membranes share several common characteristics, such as high ion conductivity (proton and lithium ion, respectively), low electronic conductivity, high thermal stability, and high chemical/electrochemical stability. Decreasing the membrane thickness but preserving the properties described above would improve the performance of the systems. Hybrid organic-inorganic nanostructured membranes can be designed to incorporate all these properties (Mosa and Aparicio 2012).

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Hybrid Processes

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In membrane science, hybrid processes are processes, in which membrane technology is combined with conventional separation equipment to perform a separation more efficiently. The objective is to combine the positive characteristics of each individual technology to obtain a process which is better than the individual process.

Reverse osmosis, gas permeation, and in particular pervaporation are the most prominent membrane processes which are combined with conventional separation equipment to form hybrid processes (Melin and Rautenbach 2007). Conventional separation equipment is either limited by equilibrium and kinetics (e.g., amine) or by thermodynamic equilibrium only (e.g., cryogenic). However, the membrane separation is controlled by kinetics. Hence, combining both the equilibrium and the kinetic limited separation can have outstanding advantages. For instance, combining a distillation column and a pervaporation module is profitable as the pervaporation unit breaks the azeotrope and the bulk separation is performed by distillation.

Combining membrane technology and conventional separation technology can significantly reduce the equipment size. By applying hybrid processes, thermodynamic limitations can be overcome or more efficient processes can be designed regarding the capital as well as the operational costs.

There are many different process configurations, in which membranes and conventional

separation equipment can be combined. Depending on the process, membranes are applied for both, to perform the bulk separation and to polish the respective products. Hybrid processes are particularly interesting when membrane units are added to existing separation equipment. Hence, debottlenecking of processes or research activities can easily be performed without shutting down the separation process (Hömmrich and Rautenbach 1998).

Examples of Hybrid Processes

Skiborowski et al. analyzed a hybrid process in which seawater is desalinated (Skiborowski et al. 2012). Reverse osmosis modules are combined with forward-feed multi-effect distillation. For low energy costs, they identified the reverse osmosis network as the most profitable plant. For moderate energy costs and for high energy costs, the hybrid process and the multi-effect distillation are the optimal process configuration, respectively.

Baker and Lokhandwala investigated natural gas processing in detail (Baker and Lokhandwala 2008). Here, typically membrane technology and amine scrubbing compete. The carbon dioxide content in the feed gas and the feed gas flow rate determine which separation technology should be applied. Interestingly, for high carbon dioxide mole fractions and for high feed flow rates, the combination of membrane technology and amine absorption is the most efficient process configuration.

The vapor recovery of gasoline vapors from storage tanks can be done by applying rubbery gas permeation membranes and condensation equipment (Rautenbach et al. 1996). Here, the bulk separation is done by condensation and the gas is subsequently polished in a gas permeation unit. Both, the recovery of gasoline and environmental standards for the exhaust gas, have to be considered in the design of such a plant.

In the MTBE (methyl *tert*-butyl ether) production methanol, MTBE and *n*-C4 have to be separated. The separation is complex due to the formation of azeotropes (Hömmrich and

Rautenbach 1998). Two hybrid processes can be applied: one in which the mixture is fed to a pervaporation module to remove the methanol while the MTBE and the n-C4 fraction are separated in a distillation column. In the other process, the raw mixture is fed to a distillation column while the pervaporation module operates at a side draw. This latter hybrid process outclasses the conventional process, in which different distillation columns are applied.

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Hybrid Regenerated Cellulose/Loaded Lipid Nanoparticle Membranes: Preparation and Characterization

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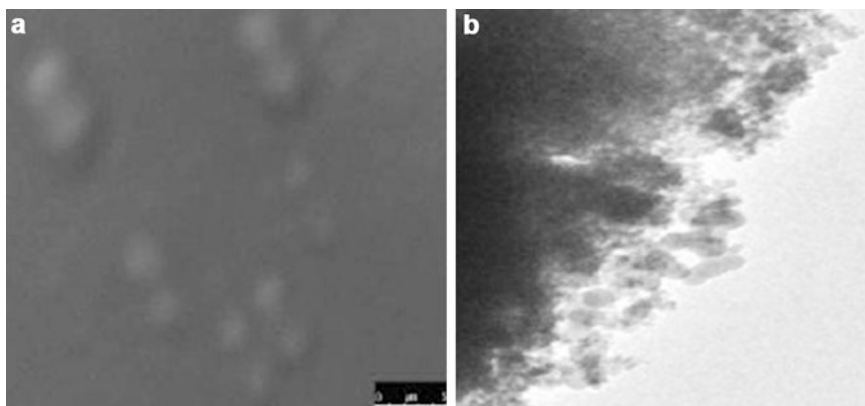
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New membrane systems related to medical applications (drug-release devices, mimetic membranes, or patches) are receiving great attention

(Müller et al. 2000). Among them, lipid nanoparticles (LNPs) prepared using biocompatible components and with tunable properties are of significant interest (Gupta and Kompella 2006; Huynh et al. 2009); although, their use is still limited due to stability problems during contact with biological fluids, storage, or administration (Korting and Schäfer-Korting 2010). To overcome these limitations, polymeric nanosphere gels were proposed for topical delivery of lipophilic molecules (Martins et al. 2007). In this context, the inclusion of functionalized lipid nanoparticles (FLNPs) in support to biocompatible membranes (such as regenerated cellulose membranes) offers an attractive route for controlled release of pharmacologic agents.

The LNPs used in this study were prepared by the ultrasound method (Feng and Huang 2001) using L- α -phosphatidylcholine and Tween[®] 80 as surfactants and glyceryl tristearate as the main lipid component, while sunscreen DHB (2,4-dihydroxybenzophenone) was the active organic component. The hybrid membrane was obtained by embedding the DHBLNPs in a dense highly hydrophilic regenerated cellulose (RC) support by immersion in a water dispersion of DHBLNPs (membrane RC/DHBLNPs). The incorporation of the loaded LNPs was characterized by AFM, brilliant field microscopy (Fig. 1a), TEM (Fig. 1b), and Raman spectroscopy (Vázquez et al. 2011; Hierrezuelo et al. 2012). Reductions in material characteristic parameters (conductivity and dielectric constant) for dry RC/DHBLNP samples when compared with the original RC and changes associated to thermal effects were also obtained.

The stability of the hybrid membrane as a result of both contact time with NaCl solutions and osmotic pressure gradients was established by comparing diffusional permeability (Ps) for original RC and RC/LNP membranes (Vázquez et al. 2011; Hierrezuelo et al. 2012). The presence of the DHBLNPs reduces in approximately 20 % Ps values for the whole interval of feed concentrations studied ($0.001 \leq C_f(M) \leq 0.4$), and a constancy in the NaCl flow for at least 20 h was also observed. The cellulose structure also reduces the DHB delivery from the



Hybrid Regenerated Cellulose/Loaded Lipid Nanoparticle Membranes: Preparation and Characterization, Fig. 1 Hybrid membrane micrographs: (a) brilliant field microscopy (b) TEM

loaded LNPs, being the value for the hybrid membrane 5 % of that for the DHBLNPs (after 30 min).

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Hybrid Silica Membranes

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A great deal of attention has been paid to silica membranes, which can accomplish separation tasks even under harsh conditions due to their high-separation performance, chemical inertness, and thermal stability (de Vos and Verweij 1998; Tsuru 2008). Two strategies have been proposed to prepare amorphous molecular sieving silica membranes: the sol–gel process and the chemical vapor deposition (CVD) method. Tetraethoxysilane (TEOS), which is a common Si precursor, has been widely adopted in both approaches, and the resultant membranes have been extensively investigated for gas separation, pervaporation, and membrane reaction. However, traditional TEOS-derived silica membranes suffer from poor hydrothermal stability, which greatly hampers their practical application. Inspired by the distinctive features of organic–inorganic hybrid silica materials with respect to flexibility, hydrothermal stability, and tunable pore sizes, researchers have concentrated on the preparation of hybrid silica membranes with improved hydrothermal stability and controlled pore sizes, using organoalkoxysilanes instead of TEOS.

Organic/inorganic hybrid membranes can be prepared either by the post-modification of hydrophilic ceramic membranes (Tsuru et al. 2004) or by the in-situ preparation using hydrophobic sols. In post-modification, hydrophilic porous membranes, the pore surface of which is covered with hydrophilic hydroxyl groups such as -SiOH , were modified with silane coupling agents such as trimethylchlorosilane in either a gas or a liquid phase, to convert the hydroxyl groups to a trimethylated surface. However, this method has several disadvantages; post-modification always reduces the effective pore sizes, leading to a decrease in flux. Moreover, it is difficult to modify membrane pores to less than several nanometers since the silane coupling agents cannot enter such small pores (Tsuru et al. 2004).

In-situ preparation of hydrophobic silica membranes was reported in sol-gel processing. Two typical kinds of organoalkoxysilanes have been used as Si precursors to prepare silica membranes via a sol-gel process. One is a bridged alkoxide, that is, a di-silicon alkoxide with a bridged group between the two silicon atoms, such as 1, 2-bis(triethoxysilyl)ethane(BTESE) $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ and bis(triethoxysilyl)methane (BTESM) $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ (Kanezashi et al. 2009; Castricum et al. 2008a, b). Castricum and coworkers (2008a; Castricum et al. 2008b) first reported on the BTESE-derived silica membrane and applied it to pervaporation dehydration of solvents of 95 wt% n-butanol-5 wt% water in an attempt to increase hydrothermal stability. The membrane was stable after 1.5 years, even though the test temperature was as high as 150 °C, while TEOS-derived silica membrane completely lost its separation ability within weeks at a much lower temperature of 95 °C. The excellent hydrothermal stability endowed by the organic-inorganic structures appears to be very promising for practical application. The formation of a looser structure and improved hydrothermal stability was due to the presence of a Si-C-C-Si minimum unit in the silica networks.

Another typical kind of organoalkoxysilane is a mono-silicon alkoxide with a pendant group, such as methyltriethoxysilane (MTES),

(trifluoropropyl)triethoxysilane (TFPTES), ethylenetriethoxysilane (ETES), or 3-methacryloxypropyltrimethoxysilane (MPS) (Raman and Brinker 1995; de Vos et al. 1999; Tsuru et al. 2011). Without burning out organic pendant groups, hybrid hydrophobic silica membranes could be obtained via the sol-gel process, which was first reported by de Vos et al. using TEOS and MTES as co-precursors (de Vos et al. 1999). The hybrid membranes prepared via this route also showed good hydrothermal stability and have been used for both gas separation and pervaporation. Considerable research on silica membranes prepared by mono-silicon alkoxides with pendant groups has led to a great deal of progress in understanding both the sol-gel process and the membrane characteristics.

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Hydraulic Resistance due to Reversible Fouling

► Reversible Fouling Resistance

Hydrocarbon Branching

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For more than 20 years now, regulations have imposed increasingly tight limitations on the content in gasoline of aromatic octane number boosters produced by the reforming of straight-run gasoline (alkanes). Among the available alternative technologies designed to enhance the octane number of straight-run gasoline, hydroisomerization is a catalytic technology that upgrades low-octane-number linear paraffins into higher-octane-number branched paraffins.

Since the rate of conversion of linear paraffins in the isomerization units is limited by a thermodynamic equilibrium, an option for increasing the production yield of dibranched paraffins consists of separating the linear and monobranched paraffins from the isomerization unit effluent and recycling them in the input of the isomerization reactor. The more conventional solution consists of fractionating the output stream from the isomerization reactor through a continuous distillation column (a deisohexanizer or DIH) into three effluents:

- A sidestream, mainly containing unconverted normal hexane and the monobranched paraffins with six carbon atoms. This stream is recycled to the isomerization unit.
- The bottom stream, containing the heaviest alkanes (paraffins) with six carbon atoms and naphthenes (cyclic paraffins) with six carbon atoms, with an RON of 82, is sent directly to the gasoline pool.

- At the top of the column, a head stream rich in dibranched paraffins with six carbon atoms, isopentane, and normal pentane. This stream, which corresponds to 90 % by weight of the fresh feed, has an RON (research octane number) of 87 though it contains about 16 % by weight of normal pentane, which has a low RON of 61.

With current distillation processes, it is not economically feasible to separate normal pentane from the other components in the top stream of the deisohexanizer since their respective boiling points are very close. This type of separation, however, can be achieved with molecular sieves, such as zeolites, implemented in cyclic adsorption processes such as a “simulated moving bed” (UOP Molex process) or “cycled pressurization/depressurization” (IFP IPSORB process or ExxonMobil ISOSIEVE process). With such processes, normal paraffins are preferentially adsorbed inside the microporosity of the zeolites and therefore separated from their branched isomers. Though offering excellent separation performance, this type of technology exhibits several drawbacks: high investment costs, sophisticated sequential operation (adsorption-desorption cycle), the use of large quantities of solvents (desorbants), and lack of modularity.

Since the beginning of the 1990s, much attention has been paid to overcoming the drawbacks of conventional zeolite adsorbents through the development of zeolite membranes that combine the technical advantages of membranes (modularity, continuous operation) with the high separation performances of zeolites (due to their sieving properties). Most of the published R&D work on that topic was carried out at lab scale mainly by academic laboratories, though a few companies, like *ExxonMobil* or *NGK Insulators*, have also published results on that topic. One of the most studied topics in this research field was the separation of normal short (C4–C6) paraffins from their branched isomers through MFI-type zeolite membranes (Arruebo et al. 2006; Bakker et al. 1996; Coronas et al. 1998). Indeed, MFI zeolites are crystalline aluminosilicates with a microporous structure that is composed of two intricate

micropore networks: elliptical straight channels with openings of 0.51×0.55 nm and zigzag channels that are almost cylindrical with a diameter of 0.53×0.56 nm, as measured by X-ray diffraction at ambient temperature (Flanigen et al. 1978). In such a confined porous system wherein the diameter of the micropores and the kinetic diameter of the diffusing molecules are close, the higher the kinetic diameter of a permeating molecule, the higher the friction of the molecule alongside the micropore wall and therefore the lower its diffusion coefficient inside the microporosity of the MFI zeolite. Therefore, the diffusion coefficient of normal alkanes in MFI zeolites is higher (Courthial et al. 2008) than the diffusion coefficient of their monobranched isomers. Moreover, these materials prove to be hardly permeable to dibranched paraffins. As an illustration, it was shown experimentally that a MFI zeolite membrane operated under close to industrial operating conditions (2–4 bar feed pressure, membrane temperature between 200 °C and 400 °C) was able to produce a permeate composed of 95 % normal pentane and 5 % isopentane from a vapor feed composed of 20 % 2,2-dimethylbutane, 55 % isopentane, and only 25 % normal pentane (Baudot and Bournay 2009).

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Hydrogel

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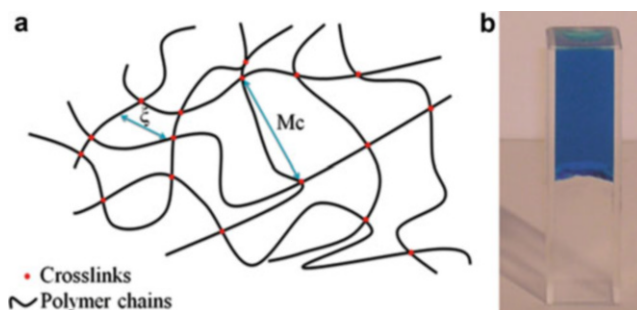
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Hydrogel

Hydrogels are cross-linked polymer systems able to retain large amounts of water by swelling. The presence in the polymeric chain of polar functional groups makes hydrogel hydrophilic systems; however, the cross-linking of the polymer matrix makes them insoluble in water (Fig. 1). The cross-linked structure can be achieved through two types of processes: chemical gelation and physical gelation. Gels with chemical bonds occur through the formation of covalent bonds among the structural units of the polymer chains and cross-linking agents (Peppas et al. 2006). The three main processes of chemical gelation are addition polymerization, condensation, and vulcanization. In contrast, the polymer chains in physical gels are connected via van der Waals forces, electrostatic attractions, and hydrogen bonds. Pectin, cellulose, agarose, collagen, and gelatin form physical gels.

Chemical and Physical Hydrogels

Initiation, propagation, and termination are the three steps of a polymerization process, i.e., the reaction among monomer molecules to form polymer chains or three-dimensional networks. During the first step of polymerization, a suitable amount of initiators, R , form by light irradiation or heat free radicals, R , which trigger the polymerization reaction as schematically shown in the following equation: $R \xrightarrow{h\nu/\Delta} R^\cdot$. These radicals can interact with a first monomer, M , and lead to the



Hydrogel, Fig. 1 (a) Structure of a hydrogel. $\overline{Mc}$ is the average molecular weight of chains between the crosslinks and ξ the average mesh size; (b) macroscopic

appearance of a hydrogel. The blue color is due to the ability of hydrogels to absorb both water and chemical compounds (in this particular case, methylene blue dye)

formation of monomers in propagation, $RM\cdot$, as shown in the following: $R\cdot + M \rightarrow RM\cdot$. Propagation consists in the growth of the polymer chain by the addition of monomers on the active site, as reported: $RM\cdots M\cdot + M \rightarrow RM\cdots MM\cdot$. Termination can halt propagation by either a disproportionation reaction or a combination reaction between two radical species.

There are different methods for the synthesis of physical gels: heating and cooling of polymer solutions (e.g., gelatin); ionic interactions (e.g., alginate); coacervation complexes by the interaction of polyanions with polycations, which form soluble complexes or insoluble depending on their concentrations and pH; hydrogen bonds, which lower the polymer solubility leading to the formation of elastic hydrogels (e.g., carboxymethyl cellulose); aging/maturation (e.g., arabic gum); and freeze-thaw. Gels with chemical bonds are provided by either polymerization of mixtures of monomers and cross-linkers or by cross-linking of preformed polymers. In the first method, a water solution of monomer, cross-linker, initiator, and catalyst is heated or irradiated to trigger the polymerization reaction. In the second method, preformed hydrophilic polymers are cross-linked by either the use of cross-linking agents (e.g., glutaraldehyde) or grafting, which functionalizes the polymer backbone with reactive species. Due to their three-dimensional structure and cross-linking centers, hydrogels swell rather than dissolve due to the diffusion of water molecules into

the polymer matrix. A polymer system initially free of water is defined as xerogel; the presence of hydrophilic groups and the degree of cross-linking establish the ability of the xerogel to store water. The greater the number of hydrophilic groups, the greater will be the ability to absorb water. The higher the degree of cross-linking, the lower the elasticity of the polymer network and the absorption of water.

Swelling Parameters

The degree of swelling is due to the equilibrium between the osmotic force, which favors the volume increase of polymer chains in the network, and the elastic forces arising from physical or covalent bonds present among the polymer chains. The swelling ratio, S_w , is a measure of how much water is retained by hydrogels and can be expressed as either the ratio between the weight of swollen gel at equilibrium, W_s , and the weight of dry gel, W_d , i.e., $S_w = W_s/W_d$, or the ratio between the volume of swollen gel at equilibrium, V_s , and the volume of dry gel, V_d , i.e., $S_v = V_s/V_d$. The percentage of swelling, $\%S_w$, is defined as $\%S_w = (W_s - W_d)/W_d \times 100$. As a function of their swelling behavior, hydrogels can be classified into conventional hydrogels, able to absorb water when they are inserted in an aqueous media, and their equilibrium swelling is not affected by environmental parameters and stimuli-responsive hydrogels, polymeric

networks which have a different equilibrium swelling in relation to environmental stimuli such as changes in pH, temperature, ionic strength, and electromagnetic radiation. In fact, every change in the water affinity of functional groups, such as a protonation or deprotonation due to a pH variation or a thermal change of hydration, leads to a reversible change in the degree of swelling. For example, the pH-sensitive hydrogels are widely used in the pharmaceutical field for administering active drugs irritating to the gastric mucosa or to protect an acid-labile substance from the stomach acid pH, i.e., the formulation is in a shrunk state at low pH and in a swollen state at high pH values. Hydrogels can withdraw solutes from aqueous solutions and can drop them in a controlled manner (Fig. 1b). It is possible to define the partition coefficient, K , as the ratio between the solute concentration in the gel (per unit volume of gel), C_{gel} , and the solute concentration in the aqueous solution in equilibrium with the external gel, C_{bulk} , i.e., $K = C_{\text{gel}}/C_{\text{bulk}}$. The changes in the hydrogel structure are often related to the average mesh size, ξ , which can be estimated by the Flory-Rehner theory (Peppas and Merrill 1977) according to the following equation:

$$\xi = v_{2,s}^{-1/3} \left(\frac{2C_n \overline{Mc}}{Mr} \right)^{1/2} l, \text{ where } C_n \text{ is the Flory characteristic ratio, } l \text{ the length of the bond along the polymer backbone, } Mr \text{ the molecular weight of the repeating units from which the polymer chain is formed, and } \overline{Mc} \text{ is given by } \frac{1}{\overline{Mc}} = \frac{2}{\overline{Mn}} - \frac{\bar{v}/V_1 [\ln(1-v_{2,s}) + v_{2,s} + \chi_1 v_{2,s}^2]}{v_{2,r} \left[\left(\frac{v_{2,s}}{v_{2,r}} \right)^{1/3} - \left(\frac{v_{2,s}}{2v_{2,r}} \right) \right]}, \text{ where } \bar{v} \text{ is}$$

the specific volume of polymer; V_1 is the solvent molar volume; χ_1 is the polymer-solvent interaction parameter; $v_{2,s}$ and $v_{2,r}$ are the polymer volume fraction in the swollen and relaxed states, respectively; and $\overline{Mn}$ is the molecular weight of the polymer chains prepared in the absence of cross-linking agent. The mesh size can be controlled by several factors, mainly by the water quantity before cross-linking and the amount and chain length of cross-linker. Both theory and experimental data show that by

increasing the amount of cross-linker compared to the quantity of monomer, there is a reduction of pore volumes and, consequently, of mesh sizes.

Applications

According to the particular application, hydrogels can be prepared as bulk systems, sheets, membranes, and nanoparticles (Nicoletta et al. 2012). There are several interesting applications of hydrogels in many fields including biochemical engineering, microelectronics, environmental science, agro-food and packaging, regenerative medicine and drug delivery, and gas separation. Examples of applications are:

1. Immobilization of enzymes. The immobilization is the restriction of enzyme mobility in a fixed space. This technique, compared to the use of enzymes in solution, has the advantage of making easier their recovery. The enzymes can be synthesized and reused reducing costs of manufacture; it is possible to optimize the microenvironment in order to increase the enzymatic stability and the product quality. The main methods for the immobilization of enzymes are adsorption (enzyme is linked on the surface of the substrate by physical bonds), retention on the support surface by covalent bonds, and entrapment (the enzyme solution is mixed with the prepolymer solution before the polymerization process).
2. Drug delivery systems (DDS). A drug delivery system is able to carry the drug in the body and control its release maintaining the plasma concentration within the therapeutic window. With a DDS it is possible to administer lower doses of drugs and limit side effects. As an example, polyacrylamide hydrogels were used as a DDS in the sustained release of insulin and delivery of other bioactive compounds. Molecular diffusion and carrier chemically controlled erosion are generally the major mechanisms of drug release.
3. Fillers in aesthetic and reconstructive surgery. The use of minimally invasive techniques is

now well known in plastic and cosmetic surgery. An ideal filler should be safe, effective, biocompatible, nonimmunogenic, easily obtainable, nonabsorbable, low-cost, and long term storable, properties that are fulfilled by many hydrogels, e.g., polyacrylamide is well tolerated in the subcutaneous tissue and glandular tissue in the breast. Another widespread application of hydrogel is the fabrication of contact lens for the most common ametropias or ocular drug release.

4. Wound synthetic dressing. Hydrogel dressing is able to create a moist environment around the wounds and facilitate wound healing, such as burns or necrotic wounds. Hydrogels can keep clean wounds by removing necrotic and infected tissues or by release of drugs. They are commercially available in sheet forms, plasters, gauzes, and gels that can be directly applied to wounds.
5. Membrane-supported hydrogels (Di Profio et al. 2014), which combine the general advantages of crystallization in gels (reproducibility, size increase, and mechanical stability of crystals) with those of membrane-assisted crystallization (process control, optimal conditions, reduced times, and specific targets). Membrane-supported hydrogels are excellent crystallization platforms as supersaturation is generated by gradual solvent removal in vapor phase through the porous structure of both membrane support and hydrogel layer. The beneficial effect of the gels, made from mixtures of acrylamide (monomer), poly(ethylene glycol dimethacrylate) (cross-linker), N,N,N',N'-tetramethylethylenediamine (catalyst), and photoinitiator, in crystallization processes by polypropylene membranes was confirmed on two model proteins, hen's egg white lysozyme and concanavalin A. By varying the ratio between monomer and cross-linker, it was possible to change the cross-linking degree and, consequently, the pore size tuning in the most adequate way the crystallization properties. Membrane-supported hydrogels were found to increase the efficiency of the crystallization process: crystals were produced at lower protein concentrations and with enhanced diffraction properties than conventional techniques.

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Hydrogel Capsules

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Capsules are particles consisting of an inner core and a shell that covers and protects the core, prepared using polymeric hydrogels. Hydrogels constitute a three-dimensional network structure obtained from a class of synthetic and/or natural polymers which can absorb and retain significant amount of water. Water holding capacity, permeability, and biocompatibility are the most important characteristic property required by the hydrogel. The cross-links between the different polymer chains give a gel its structure (hardness) and elasticity and contribute to its stickiness. The hydrogel chemistry can be modified by controlling their polarity, surface properties, mechanical properties, and swelling behavior. Hydrogels can also be stimuli sensitive and respond to surrounding environment like temperature, pH, and presence of electrolyte (Nho et al. 2005). They can display changes in their swelling behavior of the network structure according to the external environments.

The main physical approaches used for hydrogel capsule manufacturing involve gelling

Hydrogel Capsules, Table 1 Cross-linking methods to produce hydrogels and types of polymer

Cross-linking method	Polymer
Physical cross-linking	
<i>Heating/cooling</i> Helix-formation, association of the helices, and junction zones formation Hot polymeric solution is cooled down	Gelatin, carrageenan
<i>Ionic interaction</i> Ionic polymers can be cross-linked by the addition of di- or trivalent counterions	Alginate, chitosan
<i>Complex coacervation</i> Complex coacervate gels can be formed by mixing of a polyanion with a polycation. Polymers with opposite charges stick together and form soluble and insoluble complexes depending on the concentration and pH of the respective solutions	Polyanionic xanthan with polycationic chitosan Gum arabic with gelatin
<i>H-bonding</i> H-bonded hydrogel can be obtained by lowering the pH of aqueous solution of polymers carrying carboxyl groups	Carboxymethyl cellulose
<i>Maturation (heat-induced aggregation)</i> Aggregation of the proteinaceous components, induced by heat treatment, increases the molecular weight and subsequently produces a hydrogel form with enhanced mechanical properties and water binding capability	Gum arabic
<i>Freeze-thawing</i> Microcrystals in the structure are formed due to freeze-thawing	Polyvinyl alcohol Xanthan
Chemical cross-linking	
<i>Chemical cross-linkers</i> Cross-linked chains are obtained by introducing new molecules (such as glutaraldehyde, epichlorohydrin, 1, 3-diaminopropane) between the polymeric chains	Polyvinyl alcohol Carboxymethyl cellulose
<i>Grafting</i> Polymer chains are activated by the action of chemical reagents, or high-energy radiation treatment. The growth of functional monomers on activated macroradicals leads to branching and further to cross-linking	Starch Polyvinyl alcohol
Radiation cross-linking	
Free radicals are produced in the polymer following the exposure to the high-energy source such as gamma ray, x-ray, or electron beam	Carboxymethyl cellulose Chitin, chitosan, and derivatives Starch and derivatives Alginate Hyaluronan and hyaluronic acid

the droplet phase of an emulsion or spray (Shewan and Stokes 2013). Emulsification can be used for many combinations of biopolymers and oils. Cross-linked networks of synthetic and natural polymers can be obtained by physical cross-linking, chemical cross-linking, grafting polymerization, and radiation cross-linking (Table 1). The physical cross-linking method is receiving an increased interest due to relative ease of production and the advantage of not using cross-linking agents. These agents affect the integrity of substances to be entrapped (e.g., cell, proteins, etc.) as well as the need for their removal before application. Radiation cross-linking is a widely used technique since it does not involve the use of chemical agents, therefore

retaining the biocompatibility of the biopolymer. Also, the modification and sterilization can be achieved in single step, and hence, it is a cost-effective process to modify biopolymers having their end use specifically in biomedical application.

Hydrogel capsules of many synthetic and natural polymers have been produced with their end use mainly in tissue engineering, pharmaceutical, and biomedical fields (Fernandez-Neives et al. 2011; Lima et al. 2012). Due to their high water absorption capacity and biocompatibility, they have been used in wound dressing, drug delivery, injectable polymeric systems, ophthalmic applications, and hybrid-type organs (encapsulated living cells).

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Hydrogel Membranes

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Hydrogel Membranes

A membrane can be defined as a nanostructured/functionalized system which separates two different phases and can control the exchange of chemical species and energy between them. The transport is driven by the gradient of chemical potential and the application of external forces, and the flow is regulated by fluid and membrane properties. Hydrogel membranes are selective barriers made by cross-linked polymers able to retain large amounts of water by swelling (Peppas et al. 2006). They allow the flow of certain compounds (permeate) and retain some other compounds (retentate) present in fluid mixtures. Hydrogel membranes made by naturally derived (biologic) molecules have obvious biocompatibility, cell-controlled degradability, and intrinsic cellular interaction, but they may exhibit batch

variations and limited mechanical properties. In contrast, hydrogel membranes by synthetic polymers can be prepared with precisely controlled structures and functions. However, many synthetic polymers do not degrade in physiological conditions and have to be purified from eventually present toxic chemicals. Hydrogels are extremely useful in biomedical and pharmaceutical applications for their high water content and rubbery nature, which make them similar to natural tissue and with a high degree of biocompatibility. Hydrogels can protect drugs from hostile environments, such as enzymes and low pHs. Drugs loaded into the gel matrix can be released at a predesigned rate in a desired site. The mechanism of drug release from hydrogels is generally passive diffusion of molecules, which freely diffuse out of the hydrogel matrix, but is possible to control the drug release by changing the gel structure in response to environmental stimuli, such as pH, temperature, ionic strength, and electric/magnetic field.

Tissue Remediation

In addition to drug delivery applications, hydrogel membranes are also relevant in tissue engineering and remediation, i.e., for repairing and regenerating a wide variety of tissues and organs. Hydrogel dressing is a modern synthetic dressing of wounds. Its essential characteristics are the rehydration of tissues, the cleaning of wounds by removing necrotic and infected tissues, the delivery of drugs, and the maintenance of a moist environment in order to facilitate the healing of wounds, such as burns, necrotic sores, and open and chronic wounds. Such dressings are available in a variety of forms and shapes, such as sheets, pads, and gels that can be directly applied to wounds. Commercially available hydrogel sheets do not need a secondary dressing and can be cut to fit around the wounds. Hydrogel dressings do not stick to wounds and, consequently, can be easily removed, causing less pain during changes and increasing the compliance of patients and, in particular, of children. In the field of tissue engineering, hydrogels are used as a scaffold

material for the growth and replacement of various tissues as they structurally resemble the extracellular matrix of the human body. Other applications of hydrogels include tissue-engineered matrices for skin replacement and non-load-bearing bone tissue engineering, i.e., artificial skin grafts, cartilage tissues, and tissue-engineered products. Hydrogel membranes can be prepared with different mesh sizes in order to modulate their transport properties such as flux and selectivity. Mesh size can be varied by changing material concentrations, and, in particular, the amount of cross-linking agent. Thanks to its resistance to protein adsorption, biocompatibility, and non-immunogenicity, poly(ethylene glycol), PEG, plays a significant role as a hydrophilic polymer for the preparation of hydrogel membranes used in regenerative medicine. PEG has a chemical structure which can be converted into other functional groups (methyloxyl, carboxyl, acetylene, amine, azide, vinyl sulfone, thiol, and acrylate) for conjugation of biomolecules. Cross-linked PEG hydrogels can be obtained by free radical photopolymerization of PEG acrylates, Michael-type addition, native chemical ligation, and enzymatic reaction. Among these approaches, the synthesis of PEG hydrogels through photopolymerization is the most common approach which uses light to convert PEG prepolymer solutions into cross-linked insoluble hydrogels. The major type of macromers used for photopolymerization includes PEG diacrylates, multiarm PEG acrylate, and PEG dimethacrylate. PEG hydrogels can be modified to be degradable through incorporation of degradable segments, such as polyester, polypropylene fumarate, acetal, and disulfide.

Photoresponsive Hydrogel Membranes

The category of responsive membranes hosting reactive functions includes several systems such as flat and hollow fiber membranes, nanocomposite layers, microcapsules, switchable interfaces, core-shell structures, and free-standing hydrogels. Typical photoreactive groups in polymers are azobenzene, triphenylmethane, and

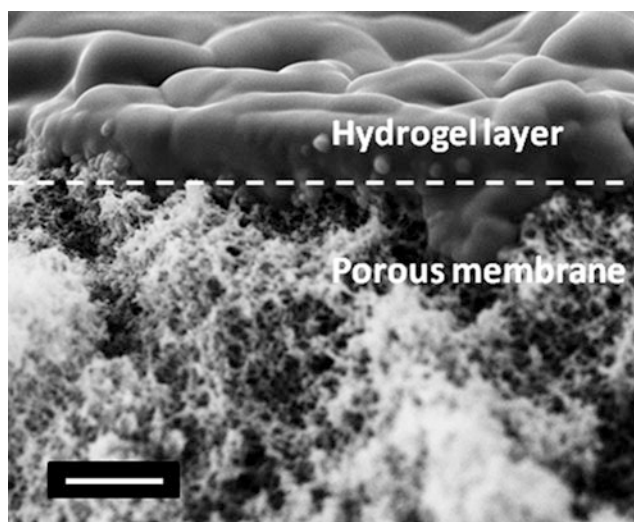
spiropyran, which can be entrapped, cross-linked, or introduced as a side chain or part of the main chain in polymer matrices (Nicoletta et al. 2012). Upon irradiation with UV-Vis light, the conformational changes of the photoreactive groups result in photoinduced effects on hydrogel matrix: pore average size changes as a consequence of expansion and contraction of the photoreactive groups. Some applications include the control of ion permeation through membrane gates (a kind of light-valved membranes that change the permeability of ions under UV irradiation) and light-controllable microfluidics. In fact, as hydrogel membranes expand in response to environmental conditions such as pH, temperature, photoirradiation, or solvent, they can facilitate the permeation of solutes, while their shrinking can suppress permeation. In particular, hydrogel brushes cast on porous membranes can open or close pores in response to environmental stimuli. An interesting application is the polyacrylamide hydrogel containing bis-[4-{dimethylamino}phenyl]{4-vinyl-phenyl} methyl leucohydroxide, which has been studied as photoresponsive and ion-selective membrane. Upon irradiation, the production of photocations increased the transport of anionic species, but had no effect on neutral species.

Membrane-Supported Hydrogels

Crystallization is, today, a fundamental operation in industry, especially pharmaceuticals, health care, and biotechnology. Efficiency, simplicity, flexibility, selectivity, permeability, compatibility, economy, stability, eco-friendship, control, and scale-up are some characteristics of membrane operations, which are important tools for the preparation, separation, crystallization, and purification of chemicals. Membrane-assisted crystallization, or shortly membrane crystallization, is an innovative technology, which allows crystal nucleation and growth under more uniform and predictable conditions favoring, in particular, compound purity, polymorphic selectivity, crystal size, and process upscale. Membrane-assisted crystallization improves significantly product characteristics and enhances process efficiency with less waste, energy, and resources. Costs are

Hydrogel Membranes,

Fig. 1 Scanning electron microscope image of a membrane-supported hydrogel. A hydrogel layer is polymerized on a porous membrane of polypropylene. Unit bar is equal to 10 μm



reduced consequently. An interesting approach is represented by membranes in combination with functionalized layers of hydrogels. This strategy includes the use of porous polymeric membranes and their functionalization with a thin hydrogel layer with an opportune mesh size (Peppas and Merrill 1977) and specific chemical composition. Cross-linked hydrogels have shown their ability to concentrate solute molecules via thermodynamic partitioning driven by favorable polymer-solute interactions. Gels generally give rise to crystals with greater sizes, fewer defects, and enhanced diffraction properties than crystals grown in solution because of the suppression of convection currents, sedimentation, and reduced random collisions between molecules. Nevertheless, the main drawback of gels is their handling difficulty, which can be passed by using adequate supports such as a membrane. In fact, earlier researches on membrane-supported hydrogels were mainly related to gel-filled pore membranes with the aim of enhancing mechanical stability, modulating transport of specific components as sketched in section “[Photoresponsive Hydrogel Membrane](#)” and reducing fouling. More recently, the possibility to fabricate membrane-supported hydrogel displaying controlled chemical composition and nanostructure to combine the general advantages of crystallization in gels (reproducibility, size increase, and mechanical stability of crystals) with those of membrane-assisted crystallization (process control, extended

optimization, reduced times, and specific targets) (Di Profio et al. 2014) has been shown. Membrane-supported hydrogels were found to be excellent crystallization platforms in which supersaturation is generated by gradual solvent removal in vapor phase through the porous structure of both membrane support and hydrogel layer (Fig. 1). The beneficial effect of the gels, made from mixtures of acrylamide (monomer), poly(ethylene glycoldimethacrylate) (crosslinker), N,N,N',N'-tetramethylethylenediamine (catalyst), and photoinitiator in membrane crystallization, was confirmed on two model proteins, chicken hen egg white lysozyme and concanavalin A. By varying the ratio between monomer and crosslinker, it was possible to change the cross-linking degree and, consequently, the pore size tuning in the most adequate way with the crystallization properties. Membrane-supported hydrogels were found to increase the efficiency of the crystallization process: crystals were produced at lower protein concentrations and with enhanced diffraction properties than conventional techniques.

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Hydrogel Nanoparticles

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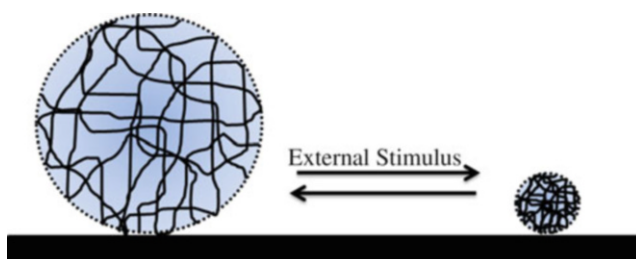
Hydrogel Nanoparticles

Hydrogel nanoparticles are nanometer-sized particles composed of cross-linked hydrophilic polymer networks (hydrogels) (Lyon and Serpe 2012; Peppas et al. 2006). They are also known as nanogels, where the term nano refers to materials, one dimension of which is less than 100 nm. The very low dimensions of nanomaterials confer them physical–chemical properties which can differ from those of the same bulk materials. As all other nanoparticles, nanogels are characterized by a high surface/volume ratio which gives them larger activities in surface-related phenomena

(e.g., adsorption, reaction rates, etc.) than hydrogel membranes. Consequently, there has been a very rapid spread of nanoparticles in many fields of daily life including fillers, cosmetics, catalysts, pharmaceuticals, sensors, lubricants, electronic devices, actuators, waste (dyes, heavy metals, and organic pollutants) remediation, advanced materials, regenerative medicine, and imaging tools (Chidichimo et al. 2013). Stimulus-responsive nanogels offer the opportunity to develop systems for applications in particular fields, such as drug delivery, biological sensing, and separation and purification technologies, thanks to their ability to undergo reversible volume phase transitions in response to environmental stimuli, such as pH, temperature, ionic strength, solvent quality, enzymes, and external electromagnetic fields (Fig. 1; Nicoletta et al. 2012). Nanogels are obtained by chemical or physical cross-linking of either synthetic or natural polymers and can be swollen/shrunk in the presence/absence of water or under the change of environmental conditions. Nanogels can be filled with molecules which can be released in opportune sites depending on the swelling/shrinking properties of nanoparticles, the erosion/degradation of polymer networks, and the reaction of chemical groups to external stimuli. These properties promote nanogels as the major carrier of drugs and contrast agents in human body. Nowadays researchers are interested in the synthesis of new hydrogel nanoparticles for applications as drug delivery systems, thermosensitive capsules, and carriers of agents for therapy and diagnostics. The main drawbacks for the use of hydrogels in many applications are the gel shrinking/swelling speed and mechanical strength. The formation of a skin layer at the very initial stage of gel shrinking

Hydrogel Nanoparticles,

Fig. 1 Volume phase transitions in nanogels in response to an external stimulus



lowers shrinking rate as it reduces the water diffusion from inside the gel to the external environment. Possible solutions to these drawbacks are the synthesis of new monomers, the modification of polymer chains (e.g., by grafting), and the use of additives (plasticizers, fillers, chemical catalysts, retarders, surfactants, etc.) in monomer solutions. In addition to nontoxicity, the response of a tissue to gel material is an important item that has to be tested carefully. In fact, different tissues (subcutis, arteries, tendons, muscles, nerves, etc.) can respond in a different way to the contact with polymer and induce its degradation with time. Other goals in nanogel research are the integration of multiple functions, the sensitivity to different stimuli, and a better control of responses. Hybrid hydrogel nanoparticles are nanometric particles with their surface properties modified by cross-linked hydrophilic polymer networks (hydrogels) in order to increase efficiency and selectivity toward particular functions or *stealth* nature of nanoparticles to the reticuloendothelial system or macrophage system.

Chemically and Physically Cross-Linked Nanogels

Nanogels can be classified as either chemically cross-linked nanogels or physically cross-linked nanogels. Chemically cross-linked nanogels are formed by cross-linking of polymers via covalent bonding. In contrast, noncovalent bonds (i.e., hydrogen bonds, ionic bonds, and hydrophobic interactions) link polymers in physically cross-linked nanogels. The most common approaches for the preparation of responsive nanogels are (i) emulsion polymerization and (ii) physical self-assembly of polymers. Emulsion polymerization generally allows controlling size, stability, and surface properties of nanogels. It involves the emulsification of hydrophobic/hydrophilic monomers in water by an oil-in-water/water-in-oil emulsifier and the initiation of reaction with either a water- or oil-soluble initiator (oil/water or water/oil emulsions). Water-in-oil emulsion polymerization is the best technique for water-soluble monomers: an aqueous solution of monomers is

mixed to the oil phase and surfactant to give thermodynamically stable micelles. Polymerization is initiated by initiators either in the aqueous phase or in the oil phase. In both oil-in-water and water-in-oil emulsion polymerization, the size of the nanogels can be controlled by varying the amount of surfactant. Smaller nanogels can be obtained by higher surfactant concentrations. However, surfactants used in emulsion polymerization have to be removed at the end of the polymerization reaction by dialysis or desorption, with possible coagulation or flocculation of nanoparticles. A way to solve this problem is the use of surfactant-free emulsion polymerization. Noncovalent interactions, such as hydrogen bonds, van der Waals forces, and electrostatic and hydrophobic interactions, allow preparing nanogels. A physical self-assembly of interactive polymers consists in amphiphilic block copolymers that self-assemble into micelles via noncovalent interactions. During the self-assembly process, small active molecules can be incorporated into the nanostructures. Nanoparticle size can be tailored by changing the block nature, block lengths, and copolymer composition. In addition, the change of other parameters, such as temperature, solvent, and additives, allows tuning the properties of aggregates. In particular, surface modifications and core functionalities of nanogels can allow the recognition of specific cells and an improved drug encapsulation. However, it is difficult to obtain stable physically cross-linked nanogels with controlled sizes using noncovalent interactions because the bonds are relatively weak.

Responsive Nanogels

A responsive nanogel is a nanoscopic three-dimensional gel network consisting of cross-linked macromolecular chains that can undergo volume phase transitions in response to an external stimulus. The thermally induced swelling or shrinking of a nanogel is caused by the thermally driven coil-to-globule transition of polymer chains (conformational change) between two neighboring cross-linking points inside the gel

network. Thermally sensitive charged nanogels can be used in protein adsorption and separation as they can form with protein complexes with a core-shell structure characterized by different properties. Interesting monomers for the synthesis of thermally responsive nanogels are those with a lower critical solution temperature in water around that of human body for their obvious applications as drug delivery systems. Poly (N-vinylcaprolactam)-based gels have a volume phase transition temperature around 33–34 °C, which can be modified by copolymerization of N-vinylcaprolactam with other monomers. In fact, copolymerization changes the hydrophilic/hydrophobic balance of the resulting polymer and consequently its critical solution temperature. In addition, copolymerization of N-vinylcaprolactam with monomers/cross-linkers allows tuning the chemical structure, size, charge, and swelling degree of nanoparticles. The biocompatibility and solubility in water solutions make poly (N-vinylcaprolactam)-based gels suitable for biomedical applications. Unlike the densely packed nanocarriers usually used for drug delivery systems, nanogels can bind within their networks a large amount of water molecules and bioactive compounds including drugs, proteins, and DNA in a relatively stable manner. These compounds can be released by the gel structure changes occurring during the volume phase transition.

Alkali-swellable nanogels containing carboxylic acids display extreme pH sensitivity and rheological changes in water. In fact, the neutralization of such aqueous dispersion causes the swelling of the nanogels with a consequent dramatic increase in viscosity and shear thinning of the dispersion. On increasing pH, the swelling increases due to the ionizing of carboxylic acid groups. In addition, the increase in ionic strength screens the internal repulsion or reduces the osmotic pressure difference between inside and outside of the nanogel particles.

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Hydrogen from Bioethanol

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The production of hydrogen from bioethanol has been considered an attractive way for exploring sustainable renewable energy sources, from an environmentally friendly point of view. Bioethanol consists of an aqueous solution containing 8–12 wt.% of ethanol, besides other by-products such as glycerol, acetaldehyde, diethyl ether, methanol, etc. (Ni et al. 2007; Iulianelli and Basile 2011).

Hydrogen production from ethanol is essentially carried out by steam reforming, according to the main reaction described by $C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$, $\Delta H(298K) = 348 \text{ kJ} \cdot \text{mol}^{-1}$. Ethanol steam reforming is a very attractive way to locally produce hydrogen, comparatively to other fuels such as methanol, glycerol, acetic acid, diethyl ether, etc. For example, ethanol is easily obtained by fermentation from renewable sources such as sugars and starches (e.g., sugarcane and corn – first-generation bioethanol) and

from lignocelluloses (agricultural, industrial, and forest residues – second-generation bioethanol), among other sources; ethanol is easy to transport and store, it is biodegradable and shows low toxicity; ethanol is relatively easy to dehydrogenate by steam reforming, and it does not contain catalyst poison such as sulfur (Ni et al. 2007).

Steam reforming of ethanol is a highly endothermic reaction, which limits its industrial application for hydrogen production. The oxidative reforming, oxidation of a fraction of ethanol to provide part of the energetic needs, is a possible way to minimize such impact. If the amount of oxygen is sufficient for balancing the reforming enthalpy needs, the process is named autothermal reforming (Song 2012). Other ways to produce hydrogen from ethanol are fermentation processes using metabolically engineered microorganisms, solar photocatalytic processes using suitable semiconductors, CO₂ dry reforming, plasma reforming, partial oxidation, and aqueous phase reforming (Song 2012).

Concerning the catalysts for the hydrogen production from (bio)ethanol, current state of the art includes the noble metal-based (Pt, Pd, Ru, Rh) and non-noble metal-based (Cu, Co, Zn, Ni) ones (Iulianelli and Basile 2011). The ethanol conversion and hydrogen yield and selectivity are strongly dependent on the catalyst type, its support (e.g., ZnO, MgO, Al₂O₃, SiO₂, La₂O₃, CeO₂), and the reaction conditions (Costa-Serra et al. 2010; Song 2012).

Besides the ethanol steam reforming main reaction referred above, the process follows a complex reaction system with several possible consecutive parallel reactions, such as partial reforming to CO, water gas shift, methanation, coke formation from intermediate products, Boudouard reaction, CO reduction, methane cracking, dehydration/hydrogenation, and

dehydrogenation. In addition to H₂ and CO₂, reformat stream may contain also CO, methane, aldehydes, ketones, ethylene, ethane, and high alcohols, among others (Vizcaíno et al. 2007; Song 2012) (Fig. 1).

The main drawback of using bioethanol to produce hydrogen via steam reforming is the high cost associated to the downstream distillation and purification steps of the crude ethanol obtained from fermentation. Feeding directly the crude bioethanol to the reformer would reduce drastically the costs of the produced hydrogen. Besides the unnecessary expensive distillation process for water and other compounds elimination, the reforming of other oxygenated hydrocarbons contained in the fermentation broth could contribute to generate extra hydrogen. The main challenge for the implementation of this approach at an industrial level remains in the tolerance and stability of the catalyst to the impurities present in the crude ethanol solution, especially high linear and branched alcohols (Le Valant et al. 2011; Song 2012).

In the viewpoint of hydrogen production for supplying polymer electrolyte membrane fuel cells (PEMFCs), the reformat stream, which comprises a complex mixture of compounds, needs a separation/purification, especially due to the maximum allowed CO concentration (0.2 ppm). A conventional steam reformer system is composed by the reformer (fixed bed reactor (FBR)), two water gas shift reactors (high- and low-temperature WGS), a CO partial oxidation reactor (PROX), and pressure swing adsorption (PSA) units (Fig. 2).

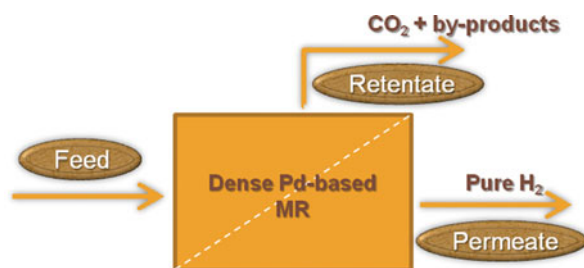
This complex process may be replaced by a much simpler membrane reactor (MR) holding hydrogen permselective membranes. This new reactor is able to perform both the steam reforming of bioethanol and the separation/



Hydrogen from Bioethanol, Fig. 2 High-purity hydrogen production in a conventional multistage system

Hydrogen from

Bioethanol, Fig. 3 High-purity hydrogen production in a membrane reactor with a Pd-based membrane



purification of the produced hydrogen in the same device (Fig. 3).

Moreover, this kind of MR makes possible the in situ removal of hydrogen from the reaction side, allowing the conversion to overcome the thermodynamic equilibrium value (which is not possible in the FBR). Furthermore, if Pd or Pd-based membranes are used, a pure hydrogen stream is collected in the permeate side, suitable for direct PEMFC supplying (Iulianelli and Basile 2011).

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Hydrogen Permeation

► H₂ Permeation Through Pd-Based Membranes

Hydrogen Production by Membrane Reactors

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Hydrogen, the energetic vector of the future, is expected to become more and more important according to leading energy scenarios as also reported in the EU-White Paper (http://ec.europa.eu/research/energy/pdf/efchp_hydrogen13.pdf) on renewable and alternative energy. Moreover, BP and GE announced plans to develop jointly up to 15 new hydrogen power plants to generate electricity over the coming decade (http://www.bp.com/content/dam/bp/pdf/investors/BP_Annual_Report_and_Form_20F_2014.pdf). The hydrogen required is planned to be derived from fossil fuels, including coal and natural gas, while developing, in the meantime, new plants equipped for carbon capture technologies capable of reducing CO₂ emissions by 90 % (<http://www.worldwatch.org/node/4516>). If one considers that, at present, 96 % hydrogen is directly produced from fossil fuels and ca. 4 % indirectly by using electricity generated through them (Kothari et al. 2008), the need to find new efficient and competitive technologies able to maximize hydrogen production

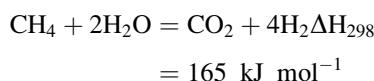
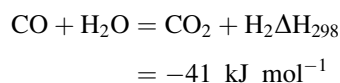
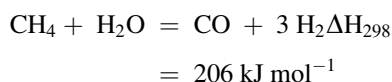
from fossil fuels while lowering CO₂ emissions and other pollutants appears evident.

In addition, up to now, steam is utilized for most H₂ obtained industrially from natural gas or light hydrocarbons. Conventional technologies can also operate with alternative fuel sources such as, for instance, bioalcohols and other biomasses, having attracted great attention owing to their being renewable sources (Abanades et al. 2013; Vizcaino et al. 2012; Sanz et al. 2014; Iulianelli et al. 2014). Along with these technologies, which can be integrated with CO₂ separation units, membrane reaction and separation units are becoming more and more promising and significant in hydrogen production. Membrane reactors couple conversion and separation in the same operating unit and this leads to a conversion higher than the thermodynamic one of conventional reactors, a lower reaction volume, a pure (permeate) hydrogen stream, and a concentrate in CO₂ (retentate) stream. The permeate hydrogen stream has a pure grade that can be directly fed without any further treatment to a polymeric electrolyte membrane fuel cell and no performance loss is observed (Brunetti et al. 2008).

Thus, the new model reactor has several advantages with respect to conventional technology, i.e., the production of a new carrier and CO₂ capture, since pure hydrogen and CO₂ concentrated streams exit this reactor.

Membrane reactors can operate in various sections of the hydrogen production plants: replacing both steam reforming (SR) as well as high- and low-temperature water gas shift (WGS) reactors.

Steam reforming is the reaction between hydrocarbons and water vapor. The steam reforming of methane is the best known of this reaction class owing to its industrial importance in hydrogen and syngas production (Scholz 1993). A methane steam reformer is industrially operated at 700–1100 °C and 20–30 bar over Ni-based catalyst; the main species and reactions involved are (Xu and Froment 1989a, b)



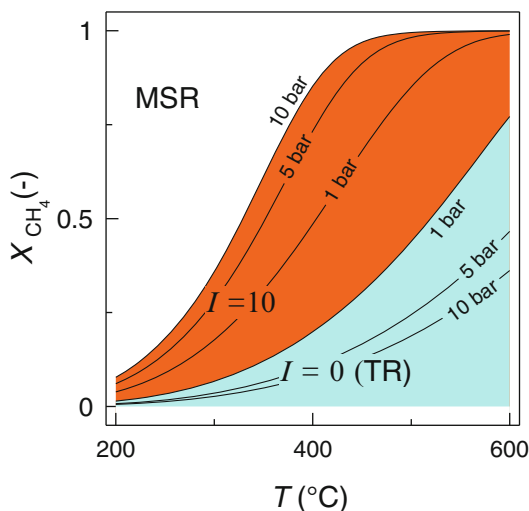
High temperature and low pressure thermodynamically favor the process because the reaction is endothermic and also characterized by an increase in the number of moles. This reaction is thermodynamically limited and the selective hydrogen removal will increase its conversion.

The development of ceramic and supported metallic (e.g., palladium-based) membranes has promoted the investigation of the membrane reformer for a high-temperature reaction. Dense palladium-based membranes are characterized by infinite hydrogen selectivity which prevents the permeation of other species through the metallic structure of the palladium.

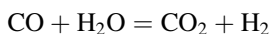
The operating conditions (temperature, pressure, flow rate, composition, etc.) have to be completely rethought since the permeation significantly affects the reforming process/reaction.

Methane steam reforming can be operated at a significantly lower temperature (400–500 °C) since the reaction pressure favors hydrogen permeation. The higher the feed pressure, the higher the hydrogen removal and as a consequence the methane conversion (see Fig. 1).

The stream produced by reformers and/or coal gasification plants contains around 50 % molar of hydrogen (on a dry basis) and between 40 % and 45 % molar of CO, which is usually reduced in an upgrading stage producing more hydrogen at the same time, by WGS reaction. The upgrading stage of traditional processes consists of a multistage CO-shift process based on two catalytic reactors: the first operates at high temperatures (about 350–400 °C) to take advantage of the faster reaction rates, whereas the other operates at low temperatures (around 220–300 °C) to refine the carbon monoxide conversion, thus allowing a lower final CO concentration (less than 1 % molar) (Raggio et al. 2005).



Hydrogen Production by Membrane Reactors, Fig. 1 Equilibrium conversion of Methane as function of the temperature for both membrane and traditional reactors at different feed pressure values for $\text{H}_2\text{O}/\text{CH}_4$ initial ratio of 3. For membrane reactor, the permeate pressure is 1 bar and the sweep contained in the permeate chamber is the times higher than the methane amount in the reaction volume. (Marigliano et al. 2001, 2003)



$$\Delta H_{298}^0 = -41 \text{ kJ mol}^{-1}$$

The H_2 -rich stream coming out from the last reactor is fed to a pressure swing adsorption (PSA) unit for H_2 separation from other gases. Most often another reaction unit is added for oxidizing CO to CO_2 , to meet the purity targets for fuel cell uses (CO concentration lower than 10–20 ppm). Additionally, the reduction of the percentage of CO in the system reduces coking of metal catalyst surfaces, implying a longer lifetime. This means an intensified process with a reduced plant size and a higher yield. In some cases, the interesting results achieved at laboratory level thanks to this effect have even led to several patents (Deckman et al. 2005; Gummalla et al. 2010; Lamm et al. 2005; Tsay et al. 2007; Wei 2009; Willms and Birdsell 2000).

However, most of the studies on WGS in MRs were carried out in a low and medium temperature range (180–250 °C and 250–320 °C, respectively) by using CuO-based catalysts, owing to the

thermodynamics constraints on the reaction (Barbieri et al. 2008; Dittmeyer et al. 2001; Mendes et al. 2010, 2011; Paglieri and Way 2002; Pinacci et al. 2010). Only few works in the literature have explored the combination of a high-temperature WGS catalyst with Pd-based membranes (Augustine et al. 2011; Bi et al. 2009; Brunetti et al. 2012, 2015; Catalano et al. 2013; Chein et al. 2013; Iyoha et al. 2007; Pinacci et al. 2010; Uemiya et al. 1991). An interesting review on the recent advances of this technology for high-temperature applications is proposed by Cornaglia et al. (2015).

Rather than the limitations of thermodynamics, fast kinetics and promoted permeation are the main advantages offered by the high temperature. However, a fundamental role is played by the characteristics of the membrane used in the reactor. In fact, until now one of the main hurdles limiting the large-scale development of these MRs is the high cost of Pd-based membranes, partly owing to the cost of palladium that could further increase if Pd membranes are exploited on a large industrial scale (Helmi et al. 2014). For this reason, great efforts are being made to obtain thin Pd layers on appropriate supports in order to maximize the permeate flux, minimize the support influence, and reduce the cost related to Pd (PachecoTanaka et al. 2005; Zhang et al. 2009).

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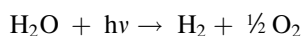
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Hydrogen Production by Water Splitting

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Hydrogen is a promising energy vector in many industries such as metallurgical industry, thermal treatments, petrochemical industry, food industry, electrical energy production, electronic industry, and mechanical industry because of the zero environmental impact of the combustion products (only water). Main sources of hydrogen are fossil (reforming of petroleum, reforming of natural gas, carbon gasification) and nuclear thermochemical and renewable processes (electrolysis from eolic and photovoltaic electrical energy, solar thermochemical processes, biomass gasification). Steam reforming of hydrocarbons is the dominant technology, but today an interesting renewable source for hydrogen production is water splitting. The theoretical energy to split water to produce H₂ and O₂ (e.g., under solar light) is



$$\Delta G = 237 \text{ kJ mol}^{-1}$$

Energy for water splitting can be supplied by various processes such as electrolysis, photochemical, photocatalytic, and thermal decomposition.

Photocatalytic water-splitting technology using nano-sized TiO₂ has great potential for low-cost, environmentally friendly solar-hydrogen production to support the future

hydrogen economy (Fujishima and Honda 1972). Presently, the solar-to-hydrogen energy conversion efficiency is too low for the technology to be economically sound. The main barriers are the rapid recombination of photo-generated electron/hole pairs and the backward reactions and the poor activation of TiO₂ by visible light (only 3–5 % of photons present in the solar light can photoactivate it). In response to these deficiencies, some investigators studied the effects of addition of sacrificial reagents and carbonate salts to prohibit rapid recombination of electron/hole pairs and backward reactions. Other research focused on the enhancement of photocatalysis by modification of TiO₂ by means of metal loading, metal ion doping, dye sensitization (O'Regan and Grätzel 1991), composite semiconductor, anion doping, and metal ion implantation. Metal ion implantation and dye sensitization are very effective methods to extend the activating spectrum to the visible range. Therefore, they play an important role in the development of efficient photocatalytic hydrogen production (Ni et al. 2007). The metal ion-implanted TiO₂ could efficiently work as a photocatalyst under visible light irradiation. Some field tests under solar light irradiation clearly revealed that the Cr ion- or V ion-implanted TiO₂ samples showed 2–3 times higher photocatalytic reactivity than the un-implanted TiO₂. Instead, a visible light-responsive TiO₂ thin-film photocatalyst, developed by a single process using a radio frequency magnetron sputtering (RF-MS) deposition method, showed high photocatalytic reactivity for various reactions such as reduction of NO_x, degradation of organic compounds, and splitting of H₂O under visible and/or solar light irradiations (Takeuchi et al. 2012). Cation- or anion-doped metal oxides or metal oxynitride was used to prepare visible light-responsive TiO₂ thin films by a radio frequency magnetron sputtering method that were applied for the separate evolution of H₂ and O₂ from water under visible or solar light irradiation (Matsuoka et al. 2007). A photochemical water-splitting system, composed by two reactors divided by a proton-conducting membrane in which photocatalytic half reactions of water reduction and water oxidation took place, was proposed by

Zamfirescu et al. Complex molecular devices based on ruthenium(bipyridine)(3)(2+) photosensitizers were dissolved in both reactors, which generate electrons or holes when exposed to high-energy photonic radiation, and acted as catalysts for water splitting. These molecular devices for water reduction have a unique property to enhance the existence time of photoelectrons, such that the likelihood of generated electron pairs to produce a molecule of hydrogen is increased (Zamfirescu et al. 2011). Thermochemical cycles using water as raw material and nuclear/renewable energies as sources of energy are believed to be a safe, stable, and sustainable route of hydrogen production. Among the well-studied thermochemical cycles, the sulfur-iodine (S-I) cycle is capable of achieving an energy efficiency of 50 %, making it one of the most efficient cycles among all water-splitting processes (Kar et al. 2012).

The S-I cycle is characterized by three basic reactions as shown below:

1. $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4$ (120 °C)
2. $2\text{H}_2\text{SO}_4 \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O} + \text{O}_2$ (830 °C)
3. $2\text{HI} \rightarrow \text{I}_2 + \text{H}_2$ (450 °C)

In order to overcome the low efficiency due to the poor equilibrium decomposition of HI in the third reaction, ongoing research is dedicated toward the development of a hydrogen-permselective membrane reactor. Proper identification of suitable membranes (e.g., asymmetric silica membrane) and introduction of membrane reactor is proposed to improve the efficiency of the overall cycle and make hydrogen production more economical. The challenges are associated toward the development of a membrane reactor which can be applied in highly corrosive environment like HI under a high temperature of about 500 °C (Kar et al. 2012). Perovskites are investigated as potential redox catalyst materials for the thermochemical production of hydrogen where water is dissociated giving rise to the production of pure hydrogen during the oxidation step. The oxidation and reduction steps can be combined in a membrane reactor constructed from dense

perovskite membranes toward a continuous and isothermal operation. At steady state and 900 °C, $25 \pm 7 \text{ cm}^3_{(\text{STP})\text{H}_2} \text{ m}^{-2} \text{ min}^{-1}$ is produced in purified state (Nalbandian et al. 2009). In a perovskite hollow-fiber membrane, the oxygen permeation flux increased 3.5 times more than that of the blank membrane when feeding reactive CH_4 onto the permeation side of the membrane. The membrane was used as a reactor to shift the equilibrium of thermal water dissociation for hydrogen production because it allows the selective removal of the produced oxygen from the water dissociation system. It was found that the hydrogen production rate increased from 0.7 to $2.1 \text{ mL}_{\text{H}_2} \text{ min}^{-1} \text{ cm}^{-2}$ at 950 °C after depositing a perovskite Pd porous layer onto the perovskite membrane (Jiang et al. 2010).

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Hydrogen Removal by Membranes

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Pure hydrogen is known to be a valuable industrial material, and its annual consumption comes to billions of cubic meters. Over 90 % of hydrogen is generated from fossil fuel sources (mainly, steam reforming of natural gas) and the other 10 % is produced by water electrolysis. Hydrogen is widely used in diverse large-scale processes in metallurgical, chemical, petrochemical, pharmaceutical, and textile industries for the production of a wide range of products – from semiconductors and steel alloys to vitamins and raw chemical materials such as ammonia, methanol, and hydrogen peroxide. Recently, hydrogen has attracted a keen attention as an alternative energy carrier for the solution of environmental problems (so-called concept of “hydrogen economy”). In contrast to fossil fuels, hydrogen combustion does not generate carbon dioxide but only water vapors. Large-scale hydrogen production requires significant capital investments for separation and purification processes; thus, the cost of hydrogen markedly increases. Conventional technologies for hydrogen separation include solvent absorption, pressure swing adsorption (PSA), fractional/cryogenic distillation, and membrane separation. Membrane separation seems to be the most promising method because of its low energy consumption, continuous operation, low investment costs, and easy operation (Ockwig and Nenoff 2007).

Among all basic large-scale applications of polymer membranes, hydrogen recovery is the most important. In the 1970s, commercial success

of hydrogen-selective hollow-fiber membrane systems for the in-process recycling of hydrogen from ammonia purge gases has triggered large-scale application of the membrane gas separation. This technology has been extended to other situations for recovery of hydrogen from gas mixtures (H₂/CO or H₂/CH₄ ratio adjustment for syngas production) and has been successfully competing with cryogenic distillation and PSA processes. In the petrochemical industry, hydrogen recovery from refinery streams is an emerging field for membrane separation; it is a key approach to meet the increased demand of hydrogen (for hydrotreating, hydrocracking, or hydrodesulfurization processes) owing to new environmental regulations (Bernardo et al. 2009).

The main liability of hydrogen-selective membranes is that recompression of the permeated hydrogen is usually required. Therefore, an alternative method involves contaminate preferential permeation, and this method is treated as a new approach for hydrogen purification, primarily by using the carbon-based membranes. For example, hydrogen production by natural gas steam reforming yields a gaseous mixture containing hydrogen and also carbon dioxide and carbon monoxide. Solubility-controlled membranes (e.g., carbon-based membranes) are preferentially permeable for big-sized gas molecules (e.g., CO₂) in relation to hydrogen. This peculiarity offers evident economic advantages that maintaining/collecting hydrogen in the retentate at nearly bulk feed pressure mitigates the demands for costly hydrogen recompression steps, even though a CO₂ compression step is required (Ockwig and Nenoff 2007).

Hydrogen-separating membranes made of palladium alloys have been developed over the past 50 years into a technology that in some instances is used in practice. In an early work in the United States and in the former Soviet Union, relatively thick-walled tubes were used. This design has been advanced for ultra-purification of hydrogen and for its application in the semiconductor manufacturing processes and in the hydrogen generators for remote or small-scale usage. Current research topics in this area are concerned with membrane reactors for hydrogen gas supply for

fuel cells or for the chemical process industry. Palladium-alloy diffusers present a key component for the recovery of hydrogen radioisotopes which are used and produced by the nuclear fission in the fusion reactors. Hydrogen recovery from waste gases or purge streams (e.g., hydrotreater off-gas) presents a potentially large application of the palladium-based membrane technology. Coal gasification or natural gas reforming coupled to a palladium membrane reactor can offer an alternative huge source of hydrogen. Production of pure hydrogen for its use in fuel cells also seems to be another important mission of the palladium-based membrane reactor (Paglieri and Way 2002).

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Hydrogen Selective Membranes

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As compared with other known fuels, hydrogen is abundantly available in the universe and possesses the highest energy content per weight unit. Moreover, in contrast to fossil fuels, the use of hydrogen as an energy source yields water as the only by-product. Hence, in recent years, the demand for hydrogen energy and production has been growing. Membrane separation process offers an attractive alternative to mature technologies such as pressure swing adsorption (PSA) and cryogenic distillation.

Hydrogen selective membranes are designed such that hydrogen concentration increases in the permeate. Based on the materials used, hydrogen selective membranes can be classified into four types: (i) polymer (organic), (ii) metallic, (iii) carbon, and (iv) ceramic. Metallic, carbon, and ceramic membranes are referred to as inorganic membranes. Depending on the type of the raw material, inorganic membranes can be classified into two groups: metal membranes and ceramic membranes. In addition, they could be divided into porous (microporous) and nonporous (dense) membranes (Adhikari and Fernando 2006). Microporous inorganic membranes include carbon and ceramic (amorphous or crystalline) membranes, and their separation characteristics are governed by the molecular sieving transport mechanism. Usually, dense inorganic membranes are based on a metal or on a polycrystalline ceramic. In these dense membranes, the fundamental operating mechanism involves the conduction of free electrons and the presence of specific catalytic surfaces in order to dissociate H_2 on the raw feed stream side and reassociate both protons and electrons on the product side. In such systems, hydrogen selectivity is typically very high because their dense structure prevents the transport of larger atoms and molecules (e.g., CO , CO_2 , O_2 , N_2 , etc.). This high selectivity provides the production of high-purity hydrogen (Ockwig and Nenoff 2007).

Historically, hydrogen separation is accomplished on the Pd-based membranes because they catalyze surface dissociation/reassociation processes and they are highly permeable to hydrogen. Palladium and Pd-alloy membranes can produce hydrogen gas on the ppb impurity levels. Since the late 1950s, small-scale Pd-based membrane modules have produced high-purity hydrogen at remote sites and for industrial, laboratory, or military purposes. There are various types of metallic membrane materials for hydrogen separation: (i) pure metals (Pd, V, Ta, Nb, and Ti); (ii) binary alloys of Pd such as Pd-Cu, Pd-Ag, Pd-Y, and also Pd-based alloys with Ni, Au, Ce, and Fe; (iii) complex alloys (Pd alloyed with three to five

other metals); (iv) amorphous alloys (typically Group IV and Group V metals); and (v) coated metals such as Pd on Ta, V, etc. (Adhikari and Fernando 2006). Dense ceramic membranes (e.g., perovskite, bismuth oxide, and solid electrolyte) have been developed and commercialized. Dense inorganic membranes are generally designed as a thin film on a porous inorganic support.

To overcome the relatively low permeance and high cost of dense metallic membranes, researchers are exploring the utility of high-permeance, less costly, and less selective microporous inorganic (silica or carbon or zeolite) membranes. The structure of these membranes presents a network of interconnected micropores with a diameter of ~ 0.5 nm. In general, microporous silicas show the highest hydrogen selectivities, and they exhibit the best H_2/N_2 selectivity which exceeds 10,000 for the membranes prepared by chemical vapor deposition (Ritter and Ebner 2007).

Since the 1970s, gas separation polymer membranes have been used industrially for hydrogen separation from gaseous mixtures in the United States (Ockwig and Nenoff 2007) and in the former Soviet Union (Yampolskii and Volkov 1991). Membranes made of glassy polymers (i.e., polymers with glass transition temperatures above the operating temperature) are used for removing hydrogen from gas mixtures. Examples of membrane materials for commercial polymer membranes include polyimide and polysulfone (asymmetric hollow fiber membranes) or polyvinyl trimethylsilane and cellulose acetate (asymmetric flat membranes). Such polymer membranes operate according to the solution-diffusion mechanism.

In general, hydrogen selectivity is low, moderate, and very high for polymeric, microporous inorganic, and metallic membranes, respectively. Polymeric membranes primarily operate at temperatures below 373 K, whereas carbon, silica, and dense ceramic membranes can function at higher temperatures (773–1,173 K). Metallic membranes can be used at ~ 573 –873 K.

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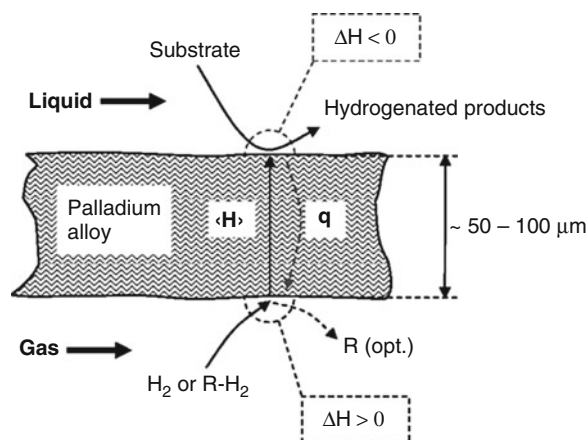
Hydrogenation Contactors and Reactors

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Among all known catalysts for hydrogenation, metals of platinum family (Pt, Pd, Ni) are known to be most efficient and advantageous. Palladium catalysts for selective hydrogenation hold the unique position. Palladium and its alloys show an excellent potential to dissolve huge amounts of hydrogen, and as membrane materials, dense palladium and palladium alloy membranes are permeable only for hydrogen.

Pioneering studies by Gryaznov and his coworkers have encouraged the use of palladium and palladium alloy membranes in catalytic membrane reactors, including fundamental studies on selective hydrogenation of various unsaturated hydrocarbons, for example, acetylene, 1,3-pentadiene, and cyclopentadiene. The general concept can be formulated as follows: hydrogen is supplied to one side of the Pd-based catalytic membrane, and then it diffuses selectively through the membrane and approaches the other side of the membrane in its highly reactive form. Fundamental concepts on membrane catalysis and catalytic membrane reactors have been advanced in the 1960s, and the phenomenon of conjugating of chemical reactions with the evolution (dehydrogenation reaction)



Hydrogenation Contactors and Reactors, Fig. 1 Principle of a dense and self-supporting palladium alloy membrane (a thin-walled tube or a foil) for liquid phase hydrogenation. Hydrogen or hydrogen-containing source R-H₂ is supplied to the gas side; a to-be-hydrogenated substrate is supplied to the liquid side.

and consumption (hydrogenation reaction) of hydrogen on palladium membranes has been discovered in 1964 (Gryaznov et al. 2003). This concept is illustrated in Fig. 1.

Early studies in this direction have been focused on the use of relatively thick nonporous Pd or Pd-alloy membranes. Their thickness can be reduced by preparation of composite membranes on porous or nonporous supports. A critically new step providing reduced consumption of expensive noble metals is concerned with the development of catalytic membranes based on the metal-polymer composites. In this case, nonporous polymer matrix, for example, silicon rubber, is loaded with palladium nanoparticles (Gryaznov et al. 2003).

Pd-based catalytic nanoparticles can be immobilized on the surface of porous inorganic or polymeric membranes, thus providing a new type of catalytic membrane reactor, called catalytic contactor. According to the proposed classification (Miachon and Dalmon 2004), depending on the mode of supply of reagents, two types of catalytic contactors exist: an interfacial contactor and a flow-through contactor. In this case, a key point is concerned with localization of reactants in the very volume where the catalyst is deposited.

The typical example of hydrogenation on an interfacial catalytic contactor is related to removal

Dehydrogenation of R-H₂ occurs on the gas-side surface and this process is endothermic; both reactions are accompanied by hydrogen transfer. Due to excellent thermal conductivity of the membrane, the heat released by hydrogenation can be utilized to facilitate endothermic dehydrogenation (autothermic operation) (Dittmeyer et al. 2004)

of dissolved oxygen (DO) from water (Volkov et al. 2011). Hydrogen and DO-containing water are supplied to the opposite sides of a hydrophobic porous catalytic membrane. In this case, membrane material should be non-wettable for water (hydrophobic) in order to provide liquid-free pores and high-rate hydrogen transmembrane mass transfer. The Pd catalyst is placed onto the water-contacting membrane surface. Water deoxygenation by catalytic membranes, including palladium-loaded hollow fibers, is accomplished by the chemical reaction between dissolved oxygen and hydrogen in the presence of the palladium catalyst.

In a flow-through contactor, reactants are forced to flow through a porous catalytic membrane, i.e., through the Pd-loaded pores. This enables to control and rule residence time of reacting species in the active zone of the catalytic membrane.

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Hydrophilic Membrane

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The hydrophilic term characterizes a membrane in relation to its behavior in an aqueous environment. The membrane's interaction with water is determined by its chemical composition and corresponding surface. Hydrophilic membranes have an affinity to water. Their surface chemistry allows these materials to be wetted immediately. Hydrophilic membrane is extremely imperative in water treatment to avoid the fouling of organic matter on the membrane surface. Diverse methods have been developed to render the hydrophobic polymeric membranes with improved hydrophilicity including surface modification and blending modification.

Hydrophilic Modification

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The developments and applications of PVDF, PSf, or other polymeric membranes are limited in the areas of purification and separation of aqueous

solution systems such as drinking water production, wastewater treatment, and bio-separation due to its hydrophobic nature. The critical problems of PVDF membrane lie in:

1. The surface energy of PVDF, which is very low, and the critical surface tension (γ_c) of PVDF, $-\text{CF}_2-$, and $-\text{CH}_2-$, which is 25 mN/m, 18 mN/m, and $\gamma_c = 31$ mN/m, respectively. This results in the poor wettability of the PVDF membrane. Therefore, the pure water flux is usually low due to the strong hydrophobic nature of PVDF.
2. The hydrophobic PVDF membrane is susceptible to fouling while treating aqueous solution containing natural organic matters, e.g., proteins. Proteins are prone to be easily absorbed onto the membrane surface or block the surface pores, decreasing the permeability and the final separation performance, depressing the lifetime of the membranes and subsequently causing more operation costs of the replacement and maintenance of the membrane modules.

One major possible reason for the protein fouling on the hydrophobic PVDF membrane is that there are almost no hydrogen bonding interactions in the boundary layer between the PVDF membrane interface and water. The repulsion of water molecules away from hydrophobic PVDF membrane surface is a spontaneous process with an increasing entropy, and therefore, protein molecules have a tendency to adsorb onto membrane surface and dominate the boundary layer. In contrast, the membrane with the hydrophilic layer possesses a high surface tension and is able to form the hydrogen bonds with surrounding water molecules to reconstruct a thin water boundary between the membrane and bulk solutions. It is difficult for hydrophobic solutes, like some proteins, to approach the water boundary and break the orderly structure because an increase of energy would be required to remove the water boundary and expose the PVDF membrane surface.

Therefore, hydrophilic modification is necessary to improve the hydrophilicity of PVDF membranes through versatile methods to enhance the lifetime and reduce the operation cost of PVDF

membranes. Different modification ways have been explored to tailor the surface engineering of the PVDF membrane in recent years. Two straightforward ways are usually used to catalogue the diverse hydrophilic and fouling resistant modification techniques, which can be mainly classified into surface modification and blending modification. Surface modification is usually achieved by coating or grafting a functional layer on the prepared membrane surface, in which most of the modified sites occurred on the top and/or bottom surface of the membrane, excluding the pores inside the membrane, due to the limited diffusion ability of the modifying agents into the membrane pores. Blending modification is usually used to achieve the desired functional properties along with the membrane preparation; therefore, the preparation and modification process can be accomplished in a single step. Both surfaces and inside pores of the membrane have a window of opportunity to be modified synchronously through the synergy effect between PVDF and compatible additives (Fu Liu 2011).

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Hydrophilic-Hydrophobic Membrane

► Amphiphilic Membrane

Hydrophilicity

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Hydrophilicity refers to a membrane with hydrophilic property. Hydrophilicity is the tendency of a

surface to become wet or to absorb water. Generally speaking, when a surface shows hydrophilicity, the molecules of water form bonds with the molecules of the surface.

In most cases, hydrophilicity refers to how readily a surface reacts with water molecules. It is also possible to measure the hydrophilicity of a surface when it comes into contact with other liquids. Understanding how hydrophilic a surface can help engineers to develop materials that show the proper amount of hydrophilicity for their intended use.

There are ways of determining hydrophilicity via utilizing precise mathematical formulas. If droplets of water remain formed on the surface and roll off easily when the surface is angled toward the ground, the material is said to be particularly hydrophobic. If, on the other hand, water is absorbed into the surface and that surface becomes wet, it is hydrophilic. The water contact angle of a hydrophilic membrane is usually below 90°.

Hydrophobic Membranes

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The hydrophobic term characterizes a membrane in relation to its behavior in an aqueous environment. The membrane's interaction with water is determined by its chemical composition and corresponding surface. Hydrophobic membranes have little or no tendency to absorb water, so that a droplet remains on the surface. The water contact angle of a hydrophobic membrane is usually over 90°.

Most polymeric membranes can be regarded as hydrophobic membranes, e.g., PVDF, PTFE, PP, PE, and PSf membranes. Hydrophobic membranes usually possess an unique advantage in membrane distillation, oil/water separation or membrane contactor.

Hydrophobic-Hydrophilic Interaction

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The hydrophobic effect is the observed tendency of nonpolar substances to aggregate in aqueous solution and exclude water molecules (IUPAC 1997; [Interfaces and the Driving Force](#) 2005). The name, literally meaning “water fearing,” describes the segregation and apparent repulsion between water and nonpolar substances. The hydrophobic effect explains the separation of a mixture of oil and water into its two components and the beading of water on nonpolar surfaces such as waxy leaves. At the molecular level, the hydrophobic effect is important in driving protein folding ([The Binding of Benzoarylsulfonamide](#) 2003), formation of lipid bilayers and micelles, insertion of membrane proteins into the nonpolar lipid environment, and protein-small molecule interactions. The hydrophobic surface is usually defined as the water drop contact angle is over 90°.

Hydrophilicity is the tendency of a surface to become wet or to absorb water. Generally speaking, when a surface shows hydrophilicity, the molecules of water form bonds with the molecules of the surface via highly dynamic hydrogen bonds. The hydrophilic surface is usually defined as the water drop contact angle is below 90°.

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Hydrophobicity

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Hydrophobicity is the term frequently used in surface chemistry describing the tendency of moving away from water or aqueous environment. The name, the combination of *hydro-* and *phobos*, simply stands for *water* and *fear* in Attic Greek. A hydrophobic surface tends not to be dissolved or wetted by water. Water forms distinct droplets on a hydrophobic surface, and their contact angles increase as its hydrophobicity increases. For more details, please refer to the section of Young’s Model.

Hydroprocessor Purge Gases

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The demand for hydrogen is constantly increasing in refineries due to more and more stringent sulfur content specifications for fuels (leading to an increasing hydrogen consumption in hydrodesulfurization processes) and a growing heavy crude consumption, which results in a higher worldwide demand for highly hydrogen-consuming upgrading processes, such as hydrocracking. In this changing landscape, permeation membranes constitute an elegant option for the recovery of hydrogen that is nowadays wasted in an array of refinery off-gases, such as fuel gas, PSA tail gas, FCC gas, catalytic reformer off-gases, or hydrocracker/hydrotreater off-gases.

Nowadays, three main membrane providers offer hydrogen purification permeators:

- *Air Products* with the *Prism*[®] silicon-coated polysulfone membranes (issued from *Monsanto*). *Air Products* claims that the life-time of the *Prism*[®] modules can be more than 15 years.
- *Ube Industries* with polyimide hollow fiber membranes.
- *Air Liquide* with the *MEDAL* polyimide and high selectivity polyaramide membranes.

All those membranes are based on glassy polymers and offer a diffusion-based hydrogen selectivity. Today's membranes have high H₂/CH₄ selectivities (from 35 to 200 at 80 °C (Roman et al. 2001)). For instance, *Air Products* claims that a single-stage array of *Prism*[®] modules is able to raise the concentration of gases from 10–30 % up to 70–90 % (*Air Products website*), while *MEDAL* membranes are able to raise the concentration of a gas at 51 bar from 86 % in hydrogen up to 98 % with a permeate pressure at 30 bar and a residue containing 52 % of hydrogen at 50 bar (*Medal website*).

In 2003, it was reported that more than 400 hydrogen permeators were installed worldwide (Monereau 2003) while approximately 100 were operated in refineries (Baker 2002). As there are more than 500 refineries in the world, it is clear that the potential market for this type of membrane applications is far from saturated. Nevertheless, three main limits still hinder the wide acceptance of permeation-based hydrogen purification in the refining industry:

- The purified hydrogen is recovered at low pressure in the permeate side and requires compression in order to feed it back to reactors. As such, PSA (pressure swing adsorption) is a more attractive process, as the produced purified hydrogen is delivered directly at high pressure.
- The sensitivity of membrane to contaminants, such as water vapor, higher hydrocarbons, or acid gases. The installation of permeators generally requires at first a very detailed analysis of the contaminants present in the feed, even at traces level, in order to design pretreatment operations. A wide array of solutions can be

Hydroprocessor Purge Gases, Table 1 Ube Industries membrane material compatibility against contaminants (*Ube Industries website*)

Contaminants	Maximum allowable content
Water vapor	Up to saturation
H ₂ S	3 % vol
NH ₃ and amines	100 ppm vol
Methanol	5 % vol
Methyl ether	5 % vol
Benzene	1 % vol
Toluene	2000 ppm vol
C ₅ + hydrocarbons	Up to saturation

used in order to remove poisonous compounds: coalescing filters in order to remove aerosols, sorbent beds, or even complete PSA (pressure swing adsorption) or TSA (temperature swing adsorption) units (Monereau 2003). This can lead to a significant increase of investment and operating costs. It should be reminded here that recent hydrogen purification membranes are still relatively tolerant to contaminants (Table 1). This is particularly true if membrane modules are operated at higher temperatures (from 80 °C to 110 °C), which results in lowering of the sorption of contaminants.

- The membrane's mechanical integrity can be damaged in transient operating conditions, especially in the case of an emergency blow-down of the membrane-based process. In certain cases, the membrane module can be submitted to pressures differences larger than its mechanical tolerance. Solution is nowadays proposed by membrane providers in order to monitor automatically the pressure balance between the feed and the permeate compartment when operating condition limits are reached (Monereau 2003).

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Hydrothermal Stability of Zeolite

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Zeolites are microporous crystalline aluminosilicates, and its Si to Al ratio and ion exchange determines its main properties. The most important application of zeolites is catalysis, and in particular zeolite Y and ZSM-5 are the catalysts in the fluid catalytic cracking (FCC) process for gasoline production in refineries. The acidity of the zeolites, related to its aluminum content and the shape selectivity given by the microporous network of cavities, are the main properties that contribute to the success of the zeolites in the cracking reactions. The production of coke in the FCC implies a continuous regeneration step at temperatures up to 800 °C in the presence of steam. Under these severe hydrothermal conditions, the activity and stability of zeolite is affected mainly due to the dealumination of the zeolite. The preparation of USY, ultrastable zeolite Y, consists of increasing the Si/Al ratio of the zeolite, decreasing the activity but increasing hydrothermal stability. Similarly the addition of phosphorous also stabilizes the aluminum framework in the zeolite (Martinez 2008). Finally the creation of the mesopores in the zeolites for FCC is also desired to crack larger molecules. The introduction of mesopores is accomplished by alkali treatment, but the thermal and hydrothermal stability again decreases, since the desilication effect of the NaOH solution, and this made some Al sites in the interior crystal become the Al sites

at the edge of the crystal, which would be extracted easily by calcination and steaming treatments. In general it could be concluded that there is a trade-off in the aluminum content of the zeolite, as it increases acidity and catalytic activity; however, hydrothermal stability decreases.

Similarly some problems related to hydrothermal stability of zeolite A, Si/Al = 1 in dehydration of organic solvent by pervaporation, has been reported. The damage effects of water on LTA zeolite membranes were verified and occur at water concentrations higher than 15 % and temperatures of 70 °C. The effects of water content in the feed and PV temperature on the membrane stability were recently investigated Li et al. (2007). The preliminary results show that the damage of LTA zeolite membrane by water mainly occurs in the grain boundary regions. The amorphous-like structure of the grain boundary is probably the principal reason for the low hydrothermal stability of LTA zeolite membrane at high water concentration, as the case of mesoporous molecular sieving materials. Solutions to this problem include the use of a zeolite with a higher Si/Al ratio, such as CHA membrane (Sato et al. 2012), and posttreatments in zeolite LTA such as silylation.

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Hydrothermal Synthesis

- [Perovskite Powder Preparation Methods](#)

Hydrothermal Synthesis of Zeolite

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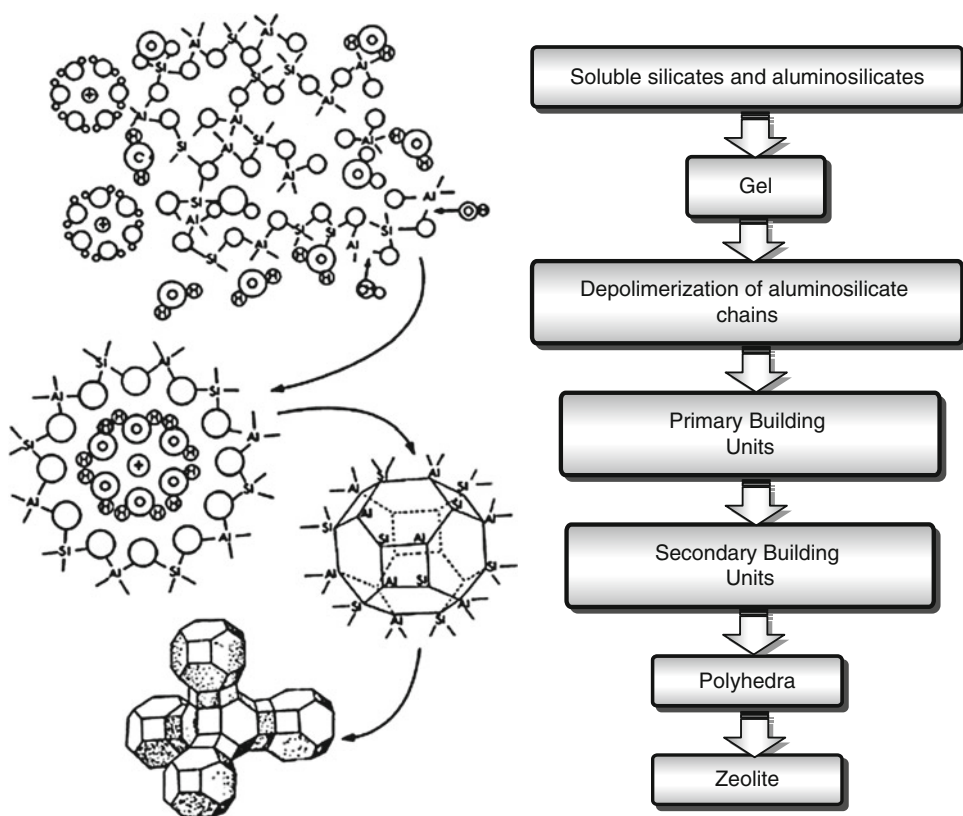
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Zeolites are crystalline, hydrated aluminosilicates having microporous, regular structures that occur naturally. The synthetic zeolites early developed by Barrer and Milton in the late 1940s (Cundy and Cox 2005) were prepared using a hydrothermal treatment at high temperature and pressure mimicking the conditions for the synthesis of these minerals in nature. There are more than 200 framework types, recognized by the International Zeolite Association (IZA, <http://www.iza-structure.org>), but only a few have been synthesized as

membranes being the most important: MFI, LTA, FAU, CHA, and MOR.

A hydrothermal treatment implies the use of an aqueous solution, synthesis gel, which is heated in an autoclave at a certain temperature under autogenous pressure. The chemicals in the synthesis gel include the silicon and aluminum sources in the presence of a mineralizing agent commonly sodium hydroxide or alternatively fluoride ion and in some cases a structure-directing agent (SDA) that facilitates the synthesis of the desired zeolite structure.

In a conventional hydrothermal synthesis all the reactants are mixed together and dissolved in the highly alkaline synthesis gel and heated up in the autoclave up to the selected temperature. After an induction period crystalline zeolite nuclei could be detected later, the nuclei start growing and finally all the amorphous material is converted into zeolite. There are several



Hydrothermal Synthesis of Zeolite, Fig. 1 Steps in Hydrothermal Synthesis of Zeolites

mechanisms proposed for the hydrothermal synthesis of zeolites (Cundy and Cox 2005), but in general they comprised the dissolution of the ionic species, organization of the aluminum and silicon tetraedra species around the structure-directing agents forming initial primary building units, that result in secondary building units, that finally form the polyhedra that comprise the zeolite structure, see Fig. 1.

The most probable mechanistic pathways in zeolite formation are described in sequence: induction period, nucleation, and crystal growth. The nucleation and crystal growth could be separated, giving rise to the ► [seeded hydrothermal synthesis method of zeolite membranes](#).

The composition of the synthesis gel influences the crystallization and the zeolite formed. Firstly the *Si/Al ratio* will define the ion exchange capacity, as one atom of Si is replaced by Al a charge defect is created. Also the hydrophobicity of the zeolite increases as the Al content increases, being zeolite A with a $Si/Al = 1$ the most hydrophilic and silicalite with $Si/Al = \infty$ the most hydrophobic. *The solvent*, as water (and sometimes alcohols) has a direct effect on the concentration of reactants, and therefore on the nucleation and growth rates. Alcohols are often added to retard the hydrolysis of the silicon alkoxide which allows controlling the crystal size by reducing the polymerization rate of the silica. The amount and nature of the solvent will also affect the viscosity of the synthesis gel, and therefore the diffusion rates of reactants during synthesis. The presence of *the structure-directing agent (SDA)*, facilitates zeolite synthesis, but in zeolite layers, and especially in membranes, may cause complications associated to template removal. *The mineralizing agents* – they also have a direct effect on the synthesis dynamics and in the hydrophilic/hydrophobic character of the resulting membranes.

The synthesis time of zeolites could vary from several hours to days in conventional ovens at temperatures ranging from 90 °C to 200 °C. It is important to mention that in the last decade the *microwave hydrothermal assisted method* (see ► [Microwave synthesis of zeolite membranes](#)) has contributed to shorten considerably synthesis

time of zeolites and zeolite membranes (Li and Yang 2008) due to a more efficient volumetric heating compared to conventional heating.

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Hydrotropes

► [Amphiphilic Molecules](#)

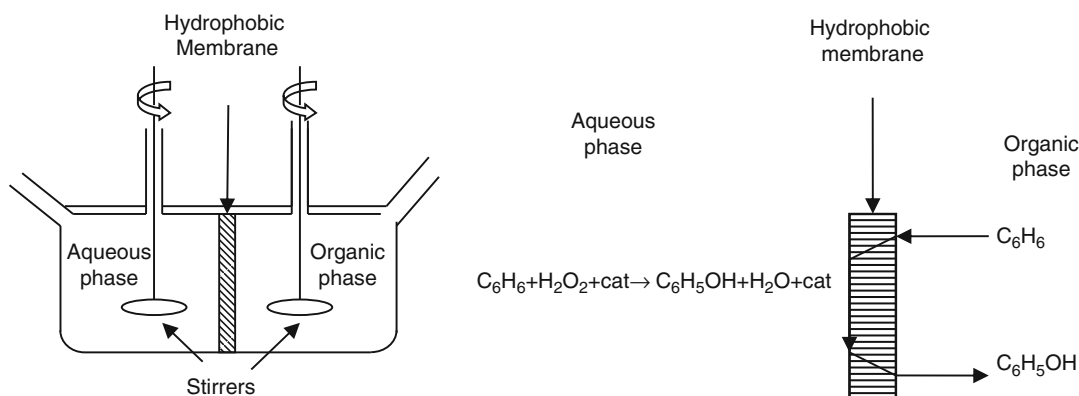
Hydroxylation of Benzene to Phenol by Membrane Contactors

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The search for new routes for phenol production based on the one-step direct benzene oxidation became more intensive because this reaction is a little selective, being the phenol more reactive than benzene, and over-oxygenated by-products occur (Molinari and Poerio 2009). To slow down consecutive catalytic reactions, a membrane contactor has been employed. This system permits to combine membrane separation and catalytic reaction in one unit operation. The separation of a product from the reaction mixture is one of the advantages in using a membrane in a reactor and permits to obtain improvements in terms of yield and selectivity in equilibrium-limited reactions and in consecutive catalytic reactions (Armor 1998).

The benzene hydroxylation to phenol was carried out in a biphasic membrane contactor (Fig. 1) in which a flat-sheet membrane separates two



Hydroxylation of Benzene to Phenol by Membrane Contactors, Fig. 1 Scheme of the membrane contactor

compartments containing two immiscible phases: an acidic aqueous phase (containing an iron catalyst and hydrogen peroxide as the oxidant) and an organic phase (only benzene).

The benzene phase, in the double task of stripping solution and reagent, avoided the use of other organic solvents with benefit in product recovery. In this system the benzene permeates across the membrane from the organic phase to aqueous membrane interface where the interfacial oxidation reaction takes place. Then the formed phenol permeates back across the membrane to the organic phase where it takes shelter from over-oxidation reaction. The high value of phenol selectivity (98 %) in the organic phase and interesting phenol productivity ($3.60 \text{ g}_{\text{ph}}\text{g}_{\text{cat}}^{-1} \text{ h}^{-1}$) were obtained, thanks to its extraction in the organic phase, avoiding further contact between phenol and the catalyst, which was soluble in the aqueous phase (Molinari et al. 2006). The drawback of this system was the low rate of phenol extraction in the organic phase. Indeed, phenol that does not cross rapidly to the membrane reacts further to generate over-oxidation products such as benzoquinone, biphenyl as trace, and tars. In order to avoid/reduce tar formation and promote phenol extraction in the organic phase, different strategies have been applied (Molinari and Poerio 2011). For example, the use of dissolved salts such as sodium sulfate in the aqueous reacting phase increased phenol extraction in the organic phase but also increased reaction kinetics, thus promoting black solid (tar) formation and

reducing the phenol productivity (0.64 gh^{-1}). The use of different operating pH values and different organic acids delayed and in some tests avoided tar formation but also gave a reduction of the phenol selectivity and then productivity. Different catalysts, such as vanadium-based vanadyl (IV) acetylacetonate (VAAC) and vanadium(III) chloride (VC), were also tested, and the obtained results evidenced improved productivity (0.97 vs $0.78 \text{ g}_{\text{ph}}\text{g}_{\text{cat}}^{-1} \text{ h}^{-1}$) using VC compared to VAA-C. No tars formation has been observed, but the system productivity was significantly lower than that obtained using an iron(II) catalyst (Molinari et al. 2012).

A direct synthesis of phenol from benzene was also studied using a photocatalytic membrane contactor (PMC), using TiO_2 as suspended catalyst (Molinari et al. 2009).

The PMC allowed to obtain the phenol production and its separation, although the formation of intermediate oxidation by-products, like benzoquinone, hydroquinone, and other oxidized molecules, was observed. Nevertheless, the acidic condition allowed to control the selectivity toward the intermediates, permitting to obtain a lower formation and extraction of the over-oxidized products.

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Hydroxypropyl Cellulose (HPC) Membrane

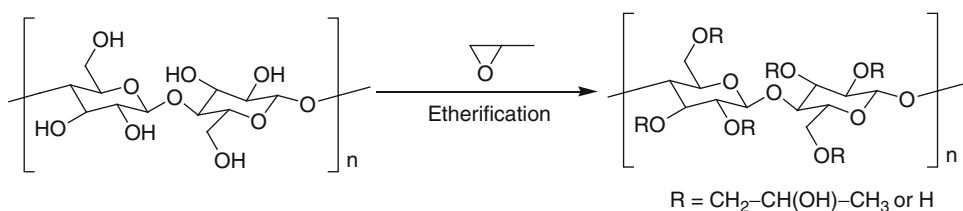
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Hydroxypropyl cellulose (HPC) is a water-soluble polymer, often used as a thickening agent, a tablet binder, and a film-coating material for drug release. Combining with ethyl cellulose (EC) or cross-linked with polyacrylic acid, HPC can be used as a mucoadhesive delivery system or oral delivery system, where the drug release rate and the drug dosage can be controlled (Kamel

et al. 2008). Figure 1 shows the synthetic route for making hydroxypropyl cellulose. The hydroxyl groups on the glucose unit of cellulose can be partially or completely substituted by hydroxypropyl groups through an etherification reaction. The maximum molar substitution is 3, and consequently, the viscosity of the polymer increases with the degree of polymerization. The broad range of accessible viscosity leads to different applications in pharmaceutical formulation, e.g., hydroxypropyl cellulose with low viscosity has been used as tablet binder, while those with medium and high viscosities have been used in the formulation of sustained-release matrices, especially in oral pharmaceutical products (Guo et al. 1998).

Due to the excellent water solubility, hydroxypropyl cellulose can be mixed with other water-soluble polymers, such as chitosan, to fabricate pervaporation membranes after cross-linking. The composite membrane has been employed to dehydrate isopropanol, with excellent flux and selectivity improvement, when compared with pure chitosan membranes (Veerapur et al. 2007).

Biocompatible hydroxypropyl cellulose has been used as a backbone in gene delivery vectors via grafting modifications, where the comb-shape copolymer exhibits low cytotoxicity and high transfection capability in a gene delivery process (Xu et al. 2009). Similarly, membranes composed of a mixture of hydroxypropyl cellulose and ethyl cellulose can offer special release profiles in drug delivery application (Sakellariou and Rowe 1995).



Hydroxypropyl Cellulose (HPC) Membrane, Fig. 1 Etherification of cellulose to hydroxypropyl cellulose (HPC)

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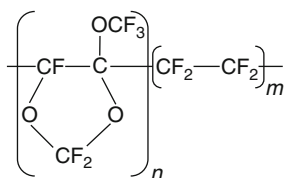
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Hyflon® AD

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Hyflon® AD is a family of amorphous perfluorinated copolymers of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-



Hyflon® AD, Fig. 1 Hyflon® AD chemical structure

Hyflon® AD,

Fig. 2 Density, glass transition, and refractive index for the two commercial grades of Hyflon® AD

Property		AD 40	AD 60
Density	g/cm ³	1.98	1.93
T _g	°C	95	125
Refractive index		1.331	1.327

dioxole (TTD) (Colaïanna et al. 1999). The chemical structure of these completely fluorinated (i.e., *perfluoro*-) copolymers is shown in Fig. 1.

Hyflon® AD and the monomers (Navarrini et al. 1999) used for its polymerization are manufactured by Solvay.

The presence of TTD units in the copolymer prevents the formation of crystalline phases (Milani et al. 2008) and completely amorphous materials are obtained when its content is higher than approximately 20 % (Arcella et al. 2003). The glass transition temperature (T_g) of Hyflon® AD copolymers increases with the content of the cyclic monomer up to 192 °C which corresponds to value of the TTD homopolymer.

The commercial grades of this amorphous perfluoropolymer are Hyflon AD® 40 and Hyflon® AD60, whose density, T_g, and refractive index are shown in Fig. 2. The numbers close to the Hyflon AD trade name indicates the molar content of TTD which is then equal to 40 % for AD40 and 60 % for AD60.

Hyflon AD® 40 is available both as high molecular weight and a low molecular weight grade, whereas Hyflon AD® 60 is produced only in one grade.

All Hyflon® AD copolymers display high solubility in fluorinated solvents and, in particular, in perfluorinated solvents like Galden® perfluoropolyethers (from Solvay) and Fluorinert® FC40 perfluorotributylamine (from 3M). This property, combined with low solution viscosity (Arcella et al. 1999), makes Hyflon® AD an ideal material for solution process technologies: uniform and thin films or coatings, down to submicron thicknesses, can be easily obtained by casting or coating techniques followed by solvent evaporations at temperatures well below the typical baking temperatures of semicrystalline perfluoropolymers.

Hyflon[®] AD copolymers combine excellent optical properties (high optical transparency, low refractive index) and a low dielectric constant with outstanding chemical and temperature resistance. They are therefore choice materials for active or protective thin layers into electronics, such as displays, wafer handling equipment, and other applications where very high optical transparency, surface contamination repellency, or static protection is required.

High transparency and high purity are the main criteria for pellicles and for electronics applications. To satisfy these demanding specifications, ultrapure grades of this material are manufactured by submitting Hyflon[®] AD to a photochemical fluorination process (Tortelli and Calini 2002) in order to completely eliminate the functional polymer end groups and any other residual contaminants that can be derived from the polymerization process.

Gas separation membranes based on Hyflon[®] AD are also of increasing interest in industrial applications (Merkel et al. 2006; Bernardo et al. 2009) due to a remarkable combination of high chemical resistance, low hydrocarbon-vapor sorption, and high resistance toward swelling and plasticization. The diffusivity of a gas through an amorphous perfluoropolymer is well described by its fractional free volumes (FFV), a common measure of the free space available, in a polymer matrix, for molecular transport, which is directly correlated to the T_g of the material. On the contrary, the higher the permeability the lower the selectivity is. Hyflon[®] AD60 having a T_g (125 °C) is a good compromise between moderately high selectivity and good permeability. Typical applications are O₂/N₂ enrichment, He/H₂ separation in space industry, and purification of natural gas.

Cross-References

- Amorphous Perfluoropolymers
- Carbon Dioxide (CO₂) Separation by Membranes
- Gas Separation
- Glass Transition Temperature (T_g)

- Membrane Swelling
- O₂/N₂ Separation

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Hyflon[®] AD Membranes

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Hyflon[®] AD membranes are made of amorphous perfluorinated copolymers produced by Solvay and composed by tetrafluoroethylene and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole units (Colaïanna et al. 1999). Hyflon[®] AD40 *high-low molecular weight*, Hyflon[®] AD40 *high molecular weight* and Hyflon[®] AD60 are three commercial grades of this family. All of them are suitable for the preparation of membranes. Even if Hyflon[®]

AD can be melt processed by molding or extrusion, the solution-based technologies are the preferred methods as they allow the preparation of thinner and more uniform membranes: spin-coating deposition and casting are used to obtain ultrathin, uniform thickness coating on flat surfaces, whereas nonplanar surfaces are more preferably coated by dipping.

By selecting the proper coating procedures, dense symmetric, asymmetric, or composite membranes can be obtained (Gordano et al. 1999; Arcella et al. 2003, 2009, 2010). Dense membranes are prepared by deposition of a thin film of the fluoropolymer solution followed by solvent evaporation, whereas asymmetric membranes are obtained by phase inversion technique: after deposition, the support coated by the fluoropolymer solution is dipped into a coagulation bath containing a non-solvent, for example, n-pentane. Composite membranes, made of a layer of the perfluorinated polymer on a porous support, like polyethersulfones and polyvinylidene fluoride (Gugliuzza and Drioli 2007; Gordano et al. 2001; Gugliuzza et al. 2006), can be prepared by coating the solution on a porous flat surface or hollow fiber (Jansen et al. 2006), followed by solvent evaporation.

Hyflon[®] AD solutions are prepared, even at concentration higher than 10 %, by dissolving the fluoropolymer powder at room temperature (or above) in Galden[®] perfluoropolyethers. These latter are a family of fluorosolvents manufactured by Solvay in several grades and characterized by different boiling points: those preferred for the preparation of membranes have a boiling point between 55 °C and 170 °C. Alternative solvents are perfluorocarbons, perfluorotriethylamine, and hydrofluoroethers.

The combination of excellent solubility and low solution viscosity, in particular for the grades AD40 *low molecular weight* and AD60, greatly simplify the purification of the fluoropolymer solutions by filtration (Arcella et al. 1999). In fact, to ensure the preparation of membranes with no defects, it is essential to avoid the presence of both suspended and dissolved contaminants.

Hyflon[®] AD membranes shows not only an extremely hydrophobic character (contact angle vs. water 120°) but also an oleophobic character, being the contact angle vs hexadecane ca. 60°, a value which implies fouling resistance.

Separation membranes based on Hyflon[®] AD are of increasing interest in industrial applications due to a remarkable combination of high chemical resistance, low hydrocarbon vapor sorption, and high resistance toward swelling and plasticization. The permeability of a gas through an amorphous perfluoropolymer is linearly correlated to its glass transition (T_g) (Arcella et al. 1999), and therefore, the higher the T_g, the higher the permeability, assuming a constant solubility coefficient. High T_g amorphous perfluoropolymers, like Teflon[®] AF (160 °C and 240 °C, two grades), offer high permeability to gases but also low selectivity. On the contrary, Hyflon[®] AD40 (T_g = 95°) and Cytop[®] (T_g = 108 °C) show lower permeability but higher selectivity. Among all the commercial amorphous perfluoropolymers, Hyflon[®] AD60, which has an intermediate T_g (125 °C), represents the best compromise between selectivity and permeability.

Gas permeability data for symmetric dense membranes of Hyflon[®] AD40 and Hyflon[®] AD60 at 35 °C and 50 psig are reported in Table 1. As previously indicated, Hyflon[®] AD 60 shows permeability higher than that of Hyflon[®] AD40. As diffusivity is attributed to the presence of voids at the molecular scale, the permeability tends to diminish with the increase of the volume of the gas molecule. Carbon dioxide, due to its paramount solubility in fluoromaterials (Kirby and McHugh 1999; McHugh et al. 1996), does not follow this rule being its permeability higher than that expected on the basis of its critical volume.

The combination of high permeability with good selectivity and with high chemical and swelling resistance makes these materials particularly useful for several applications such as gas separation, membrane contractors, membrane distillation, and pervaporation processes (Sanders et al. 2013; Bernardo et al. 2009; Gordano et al. 2001; Gugliuzza et al. 2006). Typical applications are purification of natural gas, O₂/N₂

Hyflon® AD Membranes, Table 1 Gas permeability for symmetric membranes of Hyflon AD40 and Hyflon AD60 at 35 °C and 50 psig

Gas	Critical volume (Helium = 1)	Permeability (10^{-10} cm^3 (STP) $\cdot$ $\text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$) Hyflon AD 40	Permeability (10^{-10} cm^3 (STP) $\cdot$ $\text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$) Hyflon AD 60
He	1,00	211	387
H ₂	1,13	83	182
O ₂	1,28	25	57
Ar	1,30	15	33
N ₂	1,55	8	20
CO ₂	1,62	53	128
CH ₄	1,73	4	10
C ₂ H ₄	2,25	3	6
C ₂ H ₆	2,21	2.5	3.3
C ₃ H ₈	3,50	0.94	1.1

enrichment, He/H₂ separation in space industry, and ethanol dehydration (Huang et al. 2010).

Cross-References

- ▶ Amorphous Perfluoropolymers
- ▶ Asymmetric Hollow Fiber Membranes
- ▶ Asymmetric Membrane
- ▶ Coagulation Bath
- ▶ Ethanol–Water Mixtures: Separation by Pervaporation
- ▶ Gas Separation
- ▶ Glass Transition Temperature (T_g)
- ▶ Hydrophobic Membranes
- ▶ Hydrophobicity
- ▶ Ideal Gas Selectivity
- ▶ Membrane Distillation (MD)
- ▶ Membrane Swelling
- ▶ O₂/N₂ Separation
- ▶ Pervaporation Membrane

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Hyperbranched Polyimide Membranes, Preparation and Characterization of

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Due to their structure, the macromolecular compounds can be classified as linear, branched, and

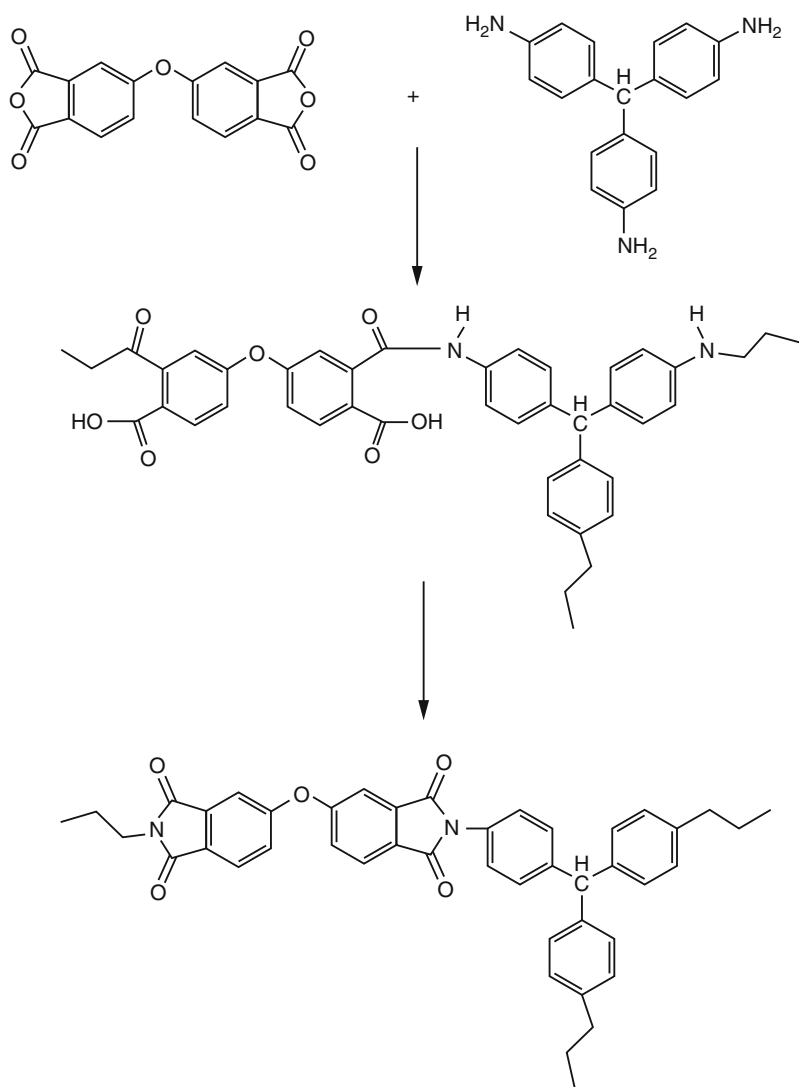
cross-linked polymers. The dendritic topology (dendrimers, hyperbranched polymers) has recently been recognized as a new class of macromolecular architecture (Tomalia 2005). Hyperbranched polymers are highly branched macromolecules. The highly branched structure and a large number of terminal functional groups are their important structural features. Hyperbranched polymers often can be simply prepared by a direct one-step polymerization of multifunctional monomers using a single-monomer (AB_x, most frequently AB₂ monomer) or double-monomer (A₂+B₃) methodology. (A and B represent two kinds of functional groups

which can react with each other but cannot undergo self-reaction.) Many kinds of hyperbranched polymers, e.g., polyesters, poly(ether ketone)s and polyamides, have been investigated as novel dendritic macromolecules so far (Gao and Yan 2004). An increasing attention has been also devoted to hyperbranched polyimides due to a potentially possible connection of the known advantages of linear or cross-linked polyimides with those of hyperbranched polymers (Jikei and Kakimoto 2004).

Polyimides exhibit very good chemical, mechanical, and dielectric stability at temperatures from $-150\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$. These rigid

Hyperbranched Polyimide Membranes, Preparation and Characterization of,

Fig. 1 Preparation of hyperbranched polyimide based on 4,4'-oxydiphthalic anhydride and 4,4',4''-triaminotriphenylmethane (via a polyimide precursor (polyamic acid))



polymers with a high glass transition temperature are mostly used in (micro)electronics, aircraft industry, and as polymeric separation membranes. Linear polyimides are traditionally prepared by two-step polymerization. The polyimide precursor, polyamic acid (the most often a solution in 1-methyl-2-pyrrolidone), is prepared from an aromatic dianhydride and aromatic diamine. This precursor is transformed into a polyimide using thermal or chemical imidization (Hergenrother 2003). It is difficult to prepare hyperbranched polyimides from AB_x monomers due to the high reactivities of A and B groups. Therefore, they are often prepared by the combination of bifunctional (A₂) and trifunctional (B₃) monomers. The ratio of anhydride and amine component determines the kind and the ratio of end groups. Nevertheless, their synthesis from trifunctional monomers often a rather complex structure requires special and controlled reaction conditions to avoid gel formation. As such triamines were used, e.g., tris(4-aminophenyl)amine or 1,3,5-tris(4-aminophenoxy)benzene (Jikei and Kakimoto (2004)).

Recently, hyperbranched polyimides were auspiciously tested as polymeric membranes for gas separation. Gas transport properties of the membranes made of 1,3,5-tris(4-aminophenoxy)benzene and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride were monitored and these properties were compared with those for linear polyimides with a similar chemical composition. The permeability, diffusivity, and solubility of the gases were higher in the membranes based on hyperbranched polyimides (Suzuki et al. 2004). Similarly, the permeability coefficients of hydrogen, carbon dioxide, oxygen, nitrogen, and methane in the membrane from the hyperbranched polyimide based on commercially available 4,4',4''-triaminotriphenylmethane and 4,4'-oxydiphthalic anhydride (Fig. 1) were 2–3.5 times higher than those in the membrane from linear polyimide based on 4,4'-diaminodiphenylmethane at comparable selectivities (e.g., oxygen/nitrogen about 6) (Minko et al. 2012). It seems that the favorable effect of both the chain character (rigidity, interactions, arrangements, higher-free volume) and selective gas sorption (cavities, end-capping groups) contributes to this increase.

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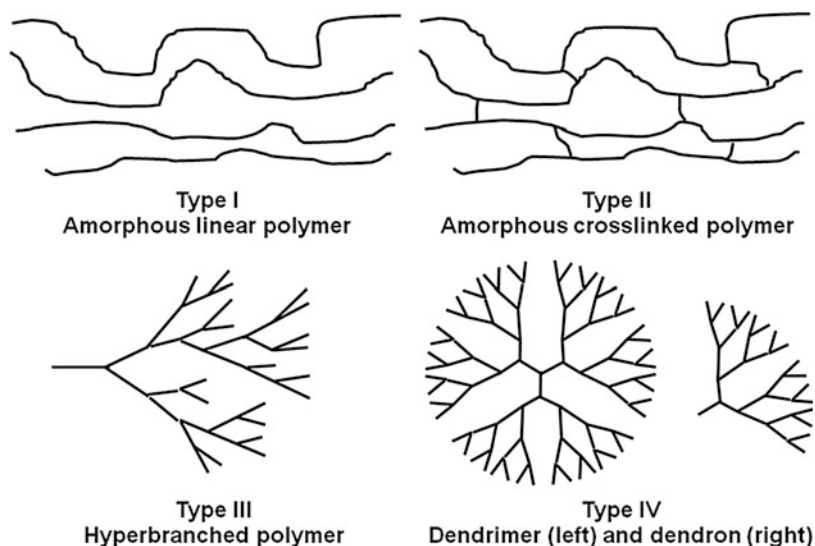
Hyperbranched Polyimides

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Hyperbranched polyimides are formed by repeated division of branches of comb polyimides. Hyperbranched polymers are synthesized by polymerization of AB₂-type monomers and consist of branched structures and mixed straight chains (Fig. 1). Rigorous structural analysis cannot be performed because branching does not regularly occur. However, hyperbranched polymers show properties differing from a normal linear polymer because entanglement of the intermolecular chains is difficult. Flory (1952) showed that gelation of polymerization of AB_x-type monomer cannot be statistically performed. Kricheldorf et al. (1982) reported the use of AB₂-type monomer as one component in copolymers, but their results lacked research attention. Hyperbranched polymers containing various

Hyperbranched Polyimides,

Fig. 1 Architecture of polymers



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repeating units have been reported since the synthesis of hyperbranched polyphenylene by one-step polymerization of AB_2 -type monomer was reported as a simple synthesis method of polymers, which were similar in structure to dendrimers by Kim and Webster (1990) of Du Pont. However, dendrimers as structurally-controlled polymers have been actively studied in the field of medicine and for use in catalytic reaction and photoreaction. Hyperbranched polymers have an obvious advantage in synthesis compared with dendrimers. Thus, these polymers can be used as an alternative to dendrimers and a low-viscosity polymer in a wide range of areas. Polyimide is a condensation polymer synthesized from dicarboxylic anhydride and primary diamine. Aromatic heterocyclic polyimides show good mechanical property and superior thermal and oxidation stability. These polyimides are widely used in place of metal and glass. They are also used for high-functional application in electrical engineering, electronic engineering, automobiles, aircraft, and packaging industry. Linear aromatic polyimides are known as polymers, which have poor workability because they are insoluble and infusible in the rigidity of the main chain structure. However, solubility for organic solvent can remarkably improve by the introduction of a multiple branching structure. Hyperbranched polyimides with

4-methylphthalimide as end groups show low dielectric constant, birefringence, and high optical transparency. These qualities result from the improvement in isotropy of molecular chains by the introduction of a multiple branching structure and inhibition of the formation of charge-transfer complex, causing coloration on linear polyimides. For aromatic amine to react easily with acid anhydride at room temperature, isolation of AB_x -type monomer with these functional groups in a molecule is difficult because of their instability. Poly(amic acid ester) is synthesized by AB_2 -type monomer, which has a carboxylic acid ester and two amino groups in a molecule and a condensation agent. Hyperbranched polyimides are synthesized by chemical imidization of poly(amic acid ester) (Yamanaka et al. 2000). Hyperbranched polyimides can be synthesized by self-polycondensation of AB_x -type monomers with imide ring in the monomer framework. Thompson et al. (1999) reported that hyperbranched polyetherimides are synthesized by thermal polycondensation of AB_2 -type monomers with fluorine (A functional group) and silylated phenolic hydroxyl group (B functional group), which can be detached in a molecule. When A_2 - and B_3 -type monomers are used as starting materials in polymerization, AB_2 -type monomers need not be synthesized. Various hyperbranched polyimides are

synthesized because they can be obtained by polymerization using a commercial A₂-type monomer and synthesized B₃-type monomer. Hyperbranched polyimides have attracted attention as materials for gas separation membranes since the early 2000s, and most of them are synthesized by A₂- and B₃-type monomers. The gas permeability of hyperbranched polyimides is almost equal to or higher than that of other glassy polymers such as polysulfone or polycarbonate.

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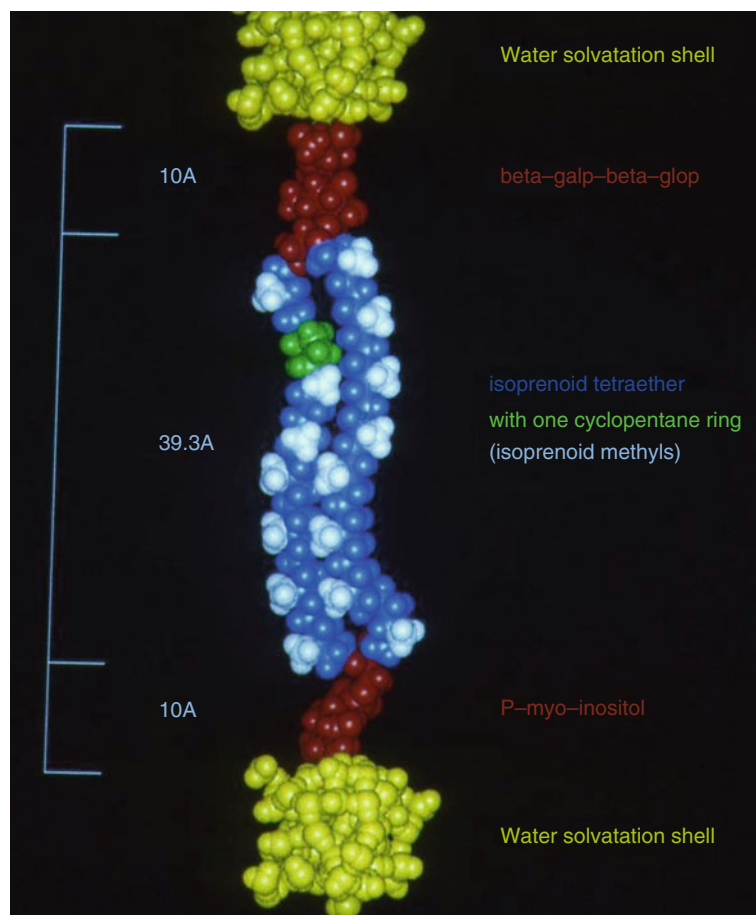
Hyperthermophiles

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Hyperthermophilic bacteria and archaea have been isolated in water-containing volcanically and geothermally heated environments situated mainly along terrestrial and submarine tectonic fracture zones and represent the organisms at the upper temperature border of life. In fact they reproduce and grow between 80 and 115 °C. Hyperthermophiles have also been isolated from hot industrial environments (e.g., the outflow of

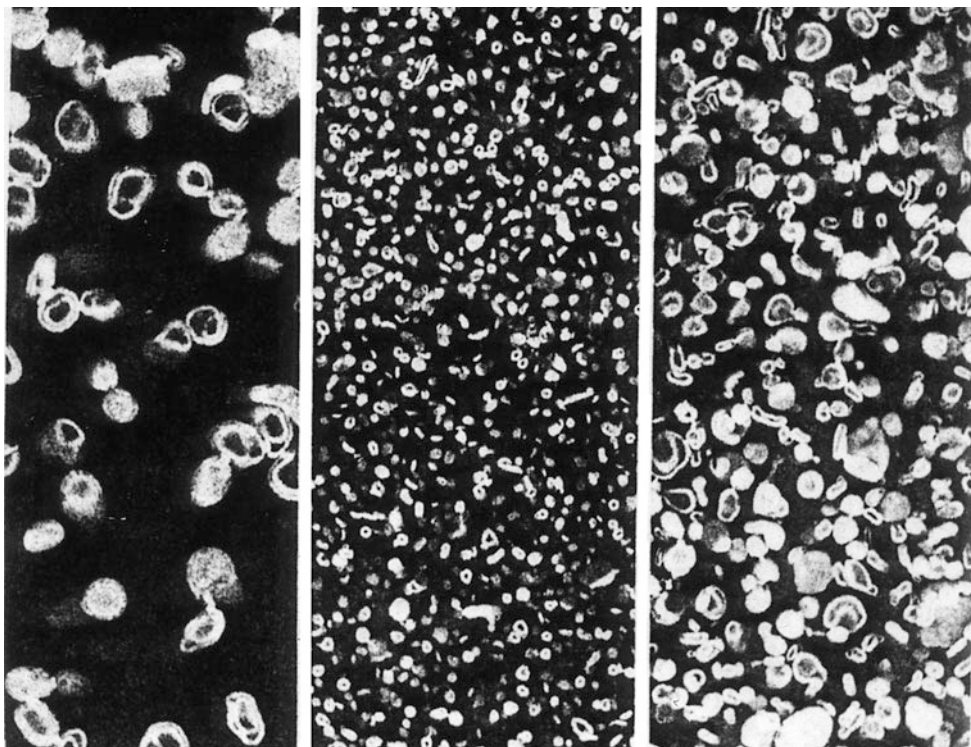
geothermal power plants and sewage sludge systems), and deep-sea biotopes present also high hydrostatic pressures (up to 360 atm); thus, the isolated species are even barophilic (Vieille and Zeikus 2001). The most heat-resistant microorganisms isolated up to date are the anaerobic archaea. The first to be identified (1960s), *Sulfolobus acidocaldarius*, a hyperthermophile and an acidophile, was found in an acidic hot spring in Yellowstone National Park, Wyoming. Since then, more than 50 hyperthermophiles have been isolated. For example, *Pyrolobus fumarii*, isolated in proximity marine hydrothermal vents, is a nitrate-reducing chemolithotroph growing in the temperature range of 90–113 °C. The upper temperature at which life is possible is still unknown, but above 110 °C, amino acids and metabolites become highly unstable. The mechanism at the base of adaptation and survival of microbes to high temperatures recently proved to involve DNA transfer (van Wolferen et al. 2013), and DNA repair through this mechanism, between the domains of bacteria and archaea, seems to have played a major role, also via homologous recombination Figs. 1 and 2. These microorganisms, because of the extreme niches in which they thrive, are adapted to distinct environmental factors including composition of minerals and gases, pH, redox potential, and salinity; most biotopes of hyperthermophiles are essentially anaerobic. Interestingly, at ambient temperatures, although unable to grow, hyperthermophiles can survive for many years by “freezing” their metabolic activities. Hyperthermophile communities are complex systems of primary producers and decomposers of organic matter. The former are chemolithoautotrophs (i.e., sulfur oxidizers, sulfur reducers, and methanogens). Because of the extremely low organic matter content of their submarine environments, hyperthermophilic heterotrophs typically obtain their energy and carbon from complex mixtures of peptides derived from the decomposition of primary producers. A few species are able to use polysaccharides (e.g., starch, pectin, glycogen, and chitin). In laboratory-scale cultivation, they needed complex medium components; hyperthermophiles reached very low cell densities, unless a specific

Hyperthermophiles,**Fig. 1** Membrane organization of hyperthermophilic archaea

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membrane bioreactor was employed. Enzymes synthesized by hyperthermophiles, also called hyperthermophilic enzymes, are typically thermostable (i.e., resistant to irreversible inactivation at high temperatures) and are optimally active at high temperatures. When cloned and expressed in mesophilic hosts, they usually retain their thermal properties, indicating that these properties are genetically encoded (Schiraldi et al. 2000). However, both sequence alignments and amino acid content comparisons show close similarities with the mesophilic counterparts suggesting that it is not a single mechanism, but a small number of highly specific alterations responsible for the remarkable stability (Cobucci-Ponzano et al. 2012). The molecular mechanisms involved in protein thermostabilization reported to date include ion pairs, hydrogen bonds, hydrophobic interactions, disulfide bridges, decrease

of the entropy of unfolding, and intersubunit interactions. Among hyperthermophilic enzymes, there are many of potential industrial interest and few that already reached commercialization. For instance, a number of hyperthermophilic proteases are now used in molecular biology and biochemistry procedures (e.g., protease S from *P. furiosus* due to the broad specificity) and numerous thermophilic restriction endonucleases. Thermophilic amylopullulanases have been suggested, as alternative enzymes to replace α -amylases during starch liquefaction for producing fermentation syrups, rich in maltose, maltotriose, and maltotetraose (DP2 to DP4) (Cobucci-Ponzano et al. 2012). However, maltodextrin biotransformation at high temperature presents various advantages. Besides the established biotechnological applications, few other potentially interesting enzymes are isolated, cloned,



Hyperthermophiles, Fig. 2 Liposomes made from archaeal lipids

and characterized, among this *S. solfataricus* paraoxonase. That proved very stable may be used for detoxification of chemical warfare agents and agricultural pesticides (Merone et al. 2005).

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Ideal Gas Selectivity

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The ideal gas selectivity of a membrane, α_{ij} , is defined as the ratio of the permeability of two pure gases, measured separately under the same conditions:

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (1)$$

where P_i and P_j are the permeability (or the permeance) of the two pure gases, respectively, with i being the most permeable gas. Rarely the real selectivity is equal to the ideal gas selectivity. Most commonly the ideal selectivity of a membrane is lower than the real selectivity, especially when the more permeable gas species plasticizes the polymer matrix, making it relatively more permeable for the slower species. In some cases, in particular in high free-volume polymers, strong sorption of the more permeable species may obstruct the transport of the less permeable species, making the mixed gas selectivity higher than the ideal selectivity.

In dense membranes, where transport occurs by the solution-diffusion mechanism, the

permeability is the product of the diffusivity and the solubility:

$$P = D \times S \quad (2)$$

where D is the diffusion coefficient and S is the solubility coefficient. Similarly, the selectivity can be expressed in a diffusion term and a solubility term:

$$\alpha_{ij} = \frac{D_i}{D_j} \times \frac{S_i}{S_j} \quad (3)$$

The ideal gas selectivity is an intrinsic property, specific for the membrane material and the particular gas pair. However, it is not a constant but it depends on the operation conditions temperature and pressure because both D and S depend on the temperature and on the operating pressure.

Ideal Separation Factor

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The separation factor, SF , is a measure of the efficiency of the separation process and is determined from the ratio of the concentrations of the

more permeable gas species i and the less permeable gas species j in the permeate divided by the ratio of the same gases i and j in the feed stream:

$$SF = \frac{x_{i,p}/x_{j,p}}{x_{i,f}/x_{j,f}} \quad (1)$$

where $x_{i,p}$ and $x_{j,p}$ are the fractions of components i and j in the permeate and $x_{i,f}$ and $x_{j,f}$ are the fractions of components i and j in the feed. The separation factor is not a material property, but it also depends on the conditions of the separation process. It depends both on the membrane properties and on the driving force, which in turn depends on the pressure and on, for instance, the presence of concentration polarization phenomena, nonideal behaviour such as plasticization, coupling effect, etc.

Analogously, the ideal separation factor is the separation factor under ideal conditions. It can be calculated from the pure gas permeabilities.

IgG Purification

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Owing to their use in the treatment of various diseases, such as primary and secondary immune deficiencies, infections, and inflammatory and autoimmune diseases, large number of immunoglobulin G (IgG) products is under clinical development. This requires certain protocols for purification and standardization. Affinity chromatography is the most popular technique to reach these requirements (Low et al. 2007). Staphylococcal protein A is one of the first affinity ligands with a very high specificity for IgG purification. It interacts with IgG through hydrophobic interactions and some hydrogen bonds and electrostatic interactions. Main disadvantages of protein A-containing carriers are the possible ligand

leakage that contaminates the therapeutic product, and also they are expensive and difficult to handle, sterilize, and preserve (Füglister 1989). Pseudo-specific ligands, such as histidine, tryptophan, phenylalanine, etc., can be used for the IgG purification. They are small molecules with high physical and chemical stability and low cost (Altıntaş and Denizli 2009; Türkmen et al. 2008). The interaction of histidine with IgG has been shown to be water mediated involving the combined electrostatic, hydrophobic, and charge-transfer interactions between histidine and the specific amino acid residues available on the protein surface (Bhattacharyya et al. 2003). In immobilized metal ion affinity chromatography (IMAC), the separation is based on the interaction of a Lewis acid (electron pair acceptor), i.e., a chelated metal ion, with electron donor atoms (N, O, and S) on the side groups of the surface histidine, tryptophan, and cysteine of the protein. Histidine-rich sequence-containing IgGs show an innate affinity for metal ions, and IMAC allows one-step separation of IgG (Altıntaş et al. 2007). Textile dyes bind proteins in a selective and reversible manner and can be used for antibody purification (Denizli and Pişkin 2001). Dye ligands can engage in ionic, hydrophobic, charge-transfer, and hydrogen bonding with proteins. In the thiophilic adsorption of proteins, electron donor-acceptor interactions between both functional groups present in the ligand structure and the adjacent sulfone group are the driving force for selective recognition (Bakhsipour et al. 2014). In general, specificity, rapid processing, mild operation conditions, conventional equipment, and reusability determine which technique to be used for IgG purification. The use of membranes has become indispensable for chromatographic applications in both research and industry area for the last few decades due to their relatively wide configuration for the size-, charge-, and affinity-based protein separation and purification. The pressure drop across the membranes is very low due to the large pore size. Owing to the continuous pore structure, mass transport occurs by convection rather than by diffusion. Chromatographic membranes are generally cost effective, and their scale-up is easier than the packed-bed

chromatography (Charcosset 1998). Membrane operations including ultrafiltration (Mohanty and Ghosh 2008; Rosenberg et al. 2009), dialysis (Bruce et al. 2002), and affinity membrane chromatography (Boi et al. 2009) have been demonstrated for their potential for IgG purification.

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Immersed Membrane Bioreactor (IMBR)

- [Submerged Membrane Bioreactor](#)

Immobilization of Enzymes

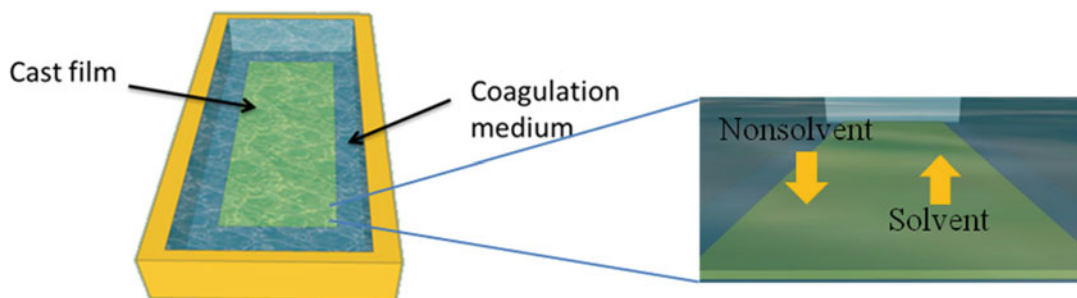
- [Biocatalytic Membrane](#)
- [Enzyme Compartmentalization](#)
- [Enzymes Immobilized on Lumen](#)

Immersion Casting

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Immersion casting is one of the most widely used methods in preparation of polymeric membranes. In this process, known as the nonsolvent-induced phase separation (NIPS) technique, the cast film is immersed in a coagulation bath, containing a nonsolvent, where the phase separation process takes place (Fig. 1). The most common nonsolvent is generally water, but aqueous solutions or pure organic solvents such as ethanol, isopropanol, or butanol can be also used. The exchange (or demixing) between the solvent, contained in the cast film, and the nonsolvent determines membrane formation by precipitation of the polymer. The cast film, after the immersion, separates into two phases: one polymer-rich phase forming the membrane matrix and one solvent-rich phase forming the pores of the membrane. Immersion casting technique is a process normally used for preparing membranes with a porous and asymmetric structure. Generally, at film surface, the pores are smaller since the phase separation occurs quickly; while at the bottom side, pores are bigger since the phase separation occurs slowly due to the tardy nonsolvent penetration. As a consequence,



Immersion Casting, Fig. 1 Cast film immersed into a coagulation medium where solvent and nonsolvent exchange occurs

the dense top layer acts as a selective barrier while the porous sublayer acts as a support giving to the membrane the mechanical resistance. The porous sublayer can exhibit different morphologies, such as spongelike or fingerlike structures, depending on the type of demixing.

A combination of factors such as the polymer concentration, the nonsolvent, and the precipitation temperature are responsible for different membrane structures. By immersion casting a range of polymeric membranes such as asymmetric porous ultrafiltration membranes and asymmetric reverse osmosis and gas separation membranes, in which the top layer is completely dense, can be produced.

Immobilized Enzyme

► Biocatalytic Membrane Reactors with Chemically Bound Enzyme

Immunoaffinity Membranes

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Immunoaffinity chromatography is a process in which the specific binding of an antigen to its specific antibody is utilized (Subramanian 2002).

The specificity of the binding makes this technique a very useful tool for the applications in which selective and strong antigen-antibody binding is advantageous. Immunoabsorption, in general, can be used for the purpose of therapy as well as preparative chromatography. Normally, the human immune system works to recognize, respond, and destroy pathogenic substances. When the ability of the immune systems to recognize foreign antigens versus healthy cells or tissues is failed, arising immune complexes, so-called autoantibodies, cause many kinds of autoimmune diseases (Massey and McPherson 2007). For example, myasthenia gravis, autoimmune hemolytic anemia and immune thrombocytopenic purpura, rheumatoid arthritis, systemic lupus erythematosus, thyroiditis, and insulin-dependent diabetes mellitus are such diseases. The immunoabsorption columns have been used for the treatment of immune diseases since the mid-1970s, in a study performed for the removal of DNA antibodies (Terman et al. 1974). Since then immunoabsorption therapy with affinity adsorbents using target specific antibodies has been increasingly utilized to remove pathogenic autoantibodies from patients' plasma (Uzun et al. 2010). Besides their use in the treatment of autoimmune diseases, immunoaffinity membranes can be used for the purification of antibodies or antigens with a high purity and also used for the selective and specific removal of toxic substances from human plasma (Denizli 2002). In such applications, membrane-based columns have advantages over traditional columns in terms of compressibility of the particles, the

fouling and slow flow rate through the column. Especially in contact with blood, stacked membrane system is desirable because of high convective transport rates without cell damage. The other desirable properties of affinity membranes are high porosity; large internal surface area; high chemical, biological, and mechanical stabilities; hydrophilicity; low nonspecific adsorption of blood proteins; and the presence of functional groups for derivatization (Denizli 2011).

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Impedance Spectroscopy

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Synonyms

Dielectric spectroscopy (DS); Electrochemical impedance spectroscopy (EIS)

Technique Description

Impedance spectroscopy (IS) technique measures the impedance (analogous to the resistance in the ideal resistor that follows Ohm's law) of a system over a wide range of frequencies. It is usually measured by applying an AC potential (or current) to an electrochemical cell and then measuring the current (or potential) response through the system. In a linear system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.

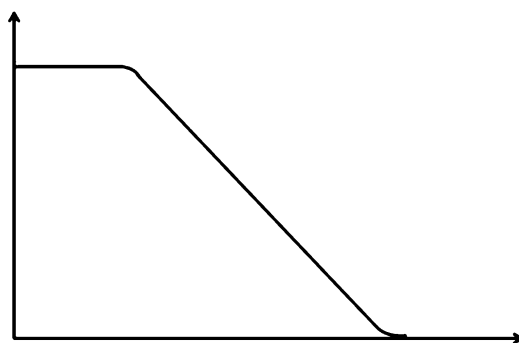
The corresponding expression representing the system impedance (Z) is indicated in Eq. 1, where ω is the radial frequency ($2\pi f$) and Φ is the phase shift. This equation can be graphically represented in a Bode plot, see Fig. 1. In a Bode plot, a logarithmic scale is used for the impedance and frequency magnitudes:

$$Z = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (1)$$

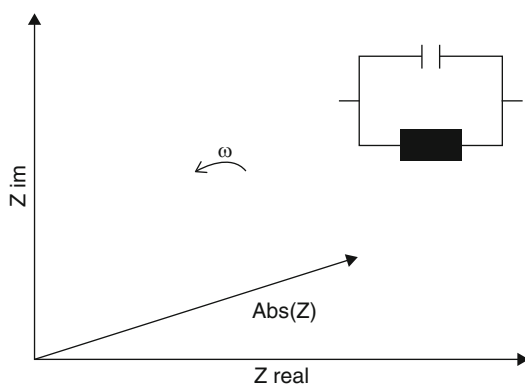
Also, the impedance is commonly expressed as a complex function:

$$Z(\omega) = Z_0(\cos \phi + j \sin \phi) \quad (2)$$

This complex expression is usually represented in a Nyquist plot. It displays the imaginary, $\text{Im}(Z)$, and the real, $\text{Re}(Z)$, contribution to the complex impedance. Figure 2 shows a Nyquist plot of the corresponding parallel RC circuit shown as well in the figure. The vector from the zero-point to any



Impedance Spectroscopy, Fig. 1 Bode plot



Impedance Spectroscopy, Fig. 2 Nyquist plot

point of the curve denotes the magnitude $|Z|$ and the phase shift, Φ . In Nyquist plot the frequency values are absent, but it decreases from right to left in the plot; each point in the plot corresponds to a frequency. The maximum of the semicircle equals occurs at such a frequency that $\omega RC = 1$, with $RC = \tau$ being the corresponding relaxation time.

More complex systems usually present a distribution of relaxation times, and the resulting Nyquist plot appears as a depressed semicircle, which is represented by a nonideal capacitor or constant phase element (CPE).

When alternating current (AC) is used in the measurements some other parasite currents can appear and disturb the experiment. This is why it is necessary to subtract these currents from the measure for each frequency. The “open” correction is made by measuring with the cell without any membrane system, with the cell containing air at the atmospheric pressure. The “short” correction has been made by using the same cell and arrangement, but the sample is a spiral copper wire in perfect contact with the electrodes without any AgCl coating. Finally, the “load” correction is obtained by using a sample with a known resistance. This open/short/load correction should be recorded and then taken into account during the measurements with the membrane system, in order to correct the values for each frequency ([Agilent Impedance Measurement Handbook 2009](#)).

Application to Membrane Characterization

Impedance spectroscopy is a powerful technique for membrane characterization. It is currently being used with different objectives: dielectric characterization (Montalvillo et al. [2011](#), [2014](#)), membrane resistance determination for ion-exchange membranes (Park et al. [2006](#)), and fouling characterization (Hu et al. [2014](#); Kavanagh et al. [2009](#)), among other specific applications.

In general, for the measurements, a membrane is placed in a cell with an electrolyte solution of specific concentration. In the cell, two electrodes are located at each side of the membrane surface, and an alternating current at a specific frequency is applied to the system which leads to an electrical potential developed through the membrane. The same procedure is repeated for a wide frequency range. In order to extract the membrane electric properties from these data it is necessary to associate the system to an equivalent electric circuit. For more complex systems, the difficulty relies on setting the proper equivalent circuit in order to obtain the electric parameters.

Following this procedure, the resistances and capacitances of the membrane are obtained and the thickness of the membrane can be evaluated. Also, by considering the dielectric constant of the solution and the membrane polymer, many membrane properties can be obtained as the resistance and capacitance values, and thus porosities and thicknesses can be obtained for each sub-layer separately as well as dielectric constant. The membrane is normally not damaged during EIS measurements (Benavente et al. [2005](#); Cañas et al. [2001](#); Cañas and Benavente [2002](#); Coster et al. [1996](#)).

Cross-References

► [Impedance Spectroscopy, Membrane Characterization by](#)

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Impedance Spectroscopy, Membrane Characterization by

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Synonyms

Electrochemical impedance spectroscopy; Impedance spectroscopy

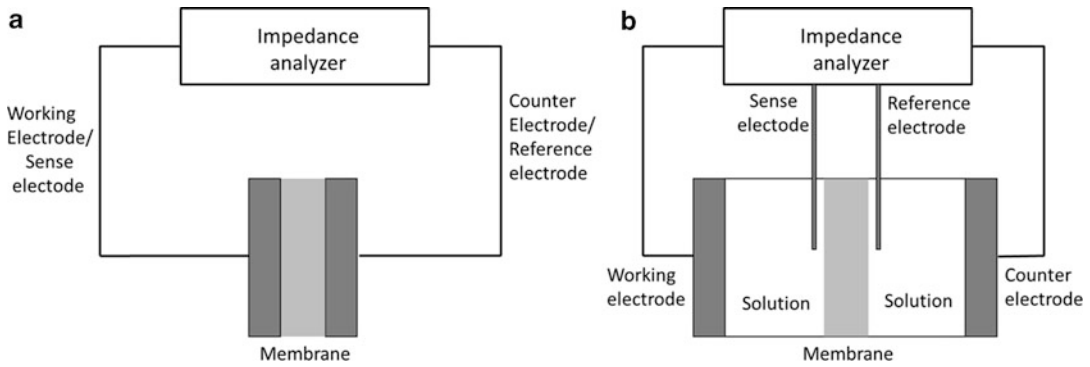
The impedance spectroscopy (IS), or electrochemical impedance spectroscopy (EIS), is a powerful technique for characterizing electrical behavior of systems in which coupled electrical processes occur at different rates (Barsoukov and Macdonald 2005). The IS technique is able to measure quantitatively the electrical resistance in the bulk and interfacial regions of solid and liquid electrolyte materials, including membranes.

IS technique is widely used in the in situ non-destructive characterization of membranes, as well as to investigate concentration polarization and fouling phenomena (Fontananova et al. 2012; Antony et al. 2013).

In EIS experiments, a sinusoidal electrical stimulus (voltage or current) is applied over a frequency range to a pair of electrodes, and the response of the system under investigation is observed by the same or different electrodes. In the first case, the configuration is indicated as a two-probe (or two electrodes) type (Fig. 1a). If two additional electrodes are used to collect the response of the system, the configuration is indicated as four-probe (or four electrodes) type (Fig. 1b). Another possible configuration uses three electrodes, but it is usually employed to characterize only one half of an electrochemical cell, or phenomena occurring on an electrode and it will not be discussed here. The two-probe configuration is usually applied when the membrane is pressed between two solid conductive electrodes, like in the case of the membrane electrode assembly (MEA) for fuel cells (Fontananova et al. 2012).

On the contrary, if the membrane is in contact with a liquid electrolyte, the four-probe configuration is the most convenient and commonly used (Antony et al. 2013). This second configuration has the advantage to eliminate the contribution of the electrode injecting stimulus/electrolyte charge transfer resistance, from the impedance spectra, focusing the probing on the membrane and its interfaces.

The sinusoidal electrical stimulus is injected through two planar electrodes (working and counter electrode), and the response of the system to the sine wave perturbation is measured by two reference electrodes (indicated as sense and



Impedance Spectroscopy, Membrane Characterization by, Fig. 1 Schematic view of the experimental setup used for membrane characterization by impedance spectroscopy using two-probes (a) and four-probes configuration (b)

reference) using an impedance analyzer (usually a potentiostat/galvanostat combined with a frequency response analyzer) which measures voltage, current, and phase shift (Fig. 1).

In analogy to Ohm's law, the impedance is defined as (Barsoukov and Macdonald 2005):

$$Z_{(\omega)} = \frac{U_{(\omega)}}{I_{(\omega)}} \quad (1)$$

where $Z_{(\omega)}$ [Ω] is the impedance, $U_{(\omega)}$ [V] is the voltage drop, $I_{(\omega)}$ [A] is the current, and they depend on the circular velocity or circular frequency ω [rad/sec] as follows:

$$U_{(\omega)} = U_o \sin \omega t \quad (2)$$

$$I_{(\omega)} = I_o \sin (\omega t + \varphi) \quad (3)$$

where $\omega = 2\pi\nu$ and ν [sec^{-1}] is the frequency, t [sec] is the time, φ [$^\circ$] is the phase shift between voltage and current, and the subscript $^\circ$ refers to the amplitude of voltage and current in phase; j is the imaginary number $j = \sqrt{-1}$.

The impedance can be also rearranged as follows:

$$Z_{(\omega)} = |Z| \cos \varphi + j|Z| \sin \varphi \quad (4)$$

The Eq. 4 indicates that the impedance is composed of two parts, i.e., the real part:

$$Z' = |Z| \cos \varphi \quad (5)$$

and the imaginary part:

$$Z'' = |Z| \sin \varphi \quad (6)$$

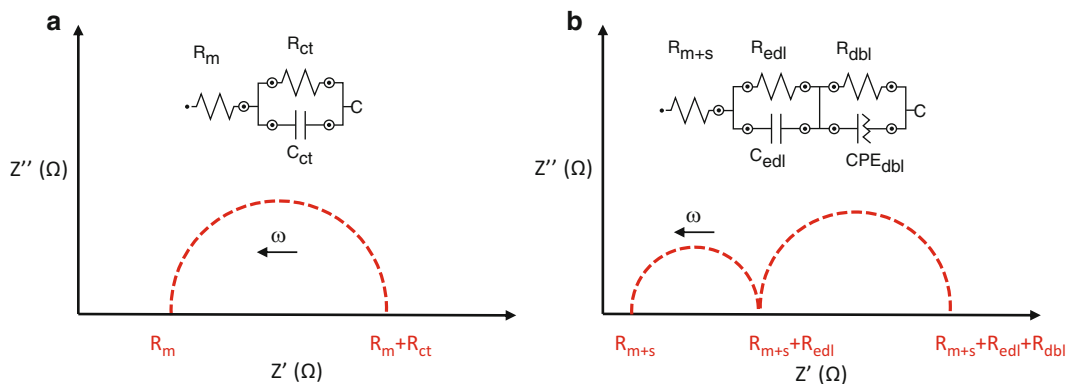
The real part of the impedance is the resistance (Z'); the imaginary part is called reactance (Z'').

On the contrary of the measurement in direct current (DC), using an alternate current (AC) over a frequency range, it is possible to distinguish phenomena proceeding at different rates, like bipolar concentration polarization of an ion exchange membrane (IEM) in contact with an electrolyte solution, which induces the formation of an electrical double layer (EDL) and a diffusion boundary layer (DBL) (Sang et al. 2008).

As a consequence, the total electrical resistance is the sum of the contribution for the transport through the membrane and the interfaces.

The bipolar concentration polarization during an AC cycle, caused by the buildup and depletion of ions at the interfaces, is time dependent. The contribution of the interfacial ionic charge transfer through the interfaces layers at low frequencies is greater than at high frequencies, because at high frequencies there is insufficient time for their formation.

The experimental impedance data can be fitted with equivalent electrical circuit models able to represent the physical system and phenomena under investigation (Zhang and Spichiger 2000).



Impedance Spectroscopy, Membrane Characterization by, Fig. 2 Impedance spectra reported as imaginary (Z'') versus real part of the impedance (Z') for an ion exchange membrane: pressed between two solid electrodes (a) and separating two electrolyte solutions (b). The spectra are registered respectively with the two- and four-probe configuration, and the corresponding equivalent circuit

models are also shown. The resistor is indicated as R, the capacitor as C, and the constant phase element (a nonideal capacitor) as CPE. The subscript “m” is referring to the membrane, “ct” to the charge transfer between electrode and membrane, “m+s” to membrane plus solution, “edl” to the electrical double layer, and “dbl” to the diffusion boundary layer

The typical shape of the impedance spectra (Z'' vs. Z') in the case of an IEM pressed between two solid electrodes exhibits a distinct arc (Fig. 2a). In the case of an IEM separating two liquid electrolyte solutions, additional semicircles appear in the spectra (Fig. 2b). The corresponding equivalent circuits are also shown in Fig. 2.

At high frequencies ($\omega \rightarrow \infty$) the intercept on the real axis gives the membrane (R_m) or membrane plus solution resistance (R_{m+s}). Of course, the solution resistance can be obtained by blank experiments (without the membrane) and its contribution can be subtracted to obtain the pure membrane resistance.

At low frequencies ($\omega \rightarrow 0$), the intercept on the real axis gives the sum of membrane (plus solution, if present) and the interface resistances.

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Imprinted Composite Membranes

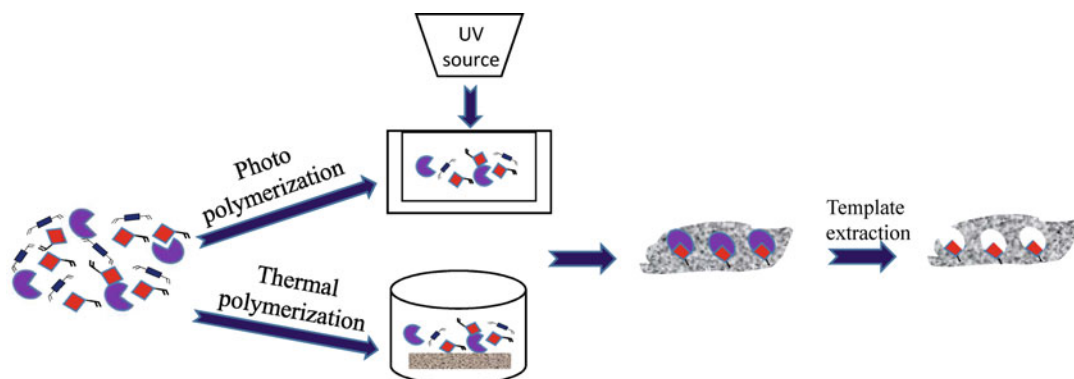
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Imprinted composite membranes represent one of the various kinds of molecularly imprinted membranes. They are produced in a form of thin films or hollow fibers from at least two different materials. The preparation of imprinted composite membranes involves the surface imprinting of a preexisting support membrane with a thin imprinted polymer layer (Xu et al. 2009). This method allows to introduce specific recognition sites into the support membrane and therefore to increase its transport selectivity. In



Imprinted Composite Membranes, Fig. 1 Schematic representation of the two surface imprinting strategies

addition, the mechanical integrity of the original membrane is preserved. The preparation of these membranes is mainly performed by exploiting two different polymerization strategies: the surface grafting via photopolymerization and the surface coating via thermopolymerization. The first route allows the copolymerization of two or more photopolymerizable monomers using the light as energy source. In the case of the thermopolymerization, the energy source is represented by the heat. Depending upon the followed route, photo- or redox initiators are used to activate the original membrane surface through the formation of radical sites. The polymerization proceeds by the addition of monomer molecules to the free radical ends of the growing polymer chains.

Figure 1 reports a schematic representation of the two surface imprinting strategies.

Composite thin imprinted membranes are also prepared by simple deposition or of imprinted polymer particles on the surface of microfiltration membranes. Cross-flow filtration can be also used to form the surface polymer layer.

A particular type of composite membranes is prepared by means of the “hybrid molecular imprinting.” This approach envisages the incorporation of a previously synthesized imprinted polymer particles into a typically used polymer matrix and the subsequent membrane formation via the phase inversion technique (Ulbricht 2004). These kinds of membranes (also called hybrid imprinted membranes) are highly selective and

exhibit higher performance with respect to membranes directly prepared with the imprinted polymer (Donato et al. 2013).

The first imprinted composite membrane was prepared in 1997 (Wang et al. 1997) using as support matrix a poly(acrylonitrile) membrane. A molecularly imprinted layer on the membrane surface was formed by means of the UV-initiated photo-copolymerization of acrylic acid and *N,N* methylenebisacrylamide. Theophylline was used as template molecule.

Due to the mechanical and chemical stability in combination with high performance, imprinted composite membranes have a large potential application, like in biosensor technology, in solid phase extraction, in microfiltration, and in enantiomeric separation.

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Imprinted Polysulfone-Aldehyde Derivatized Nanofiber Membranes

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The functionalization of aromatic polysulfones for tailoring properties in membrane applications is of great interest. Polysulfone has overall thermal and chemical stability combined with good mechanical and membrane-making qualities. Polysulfone is a stable platform for functional group attachment and a good candidate polymeric material for membranes with tailored functionalities (Guiver et al. 1999). To this end, modified polysulfones have been intensively studied in connection with chiral separation (Yoshikawa et al. 1998, 2005, 2006, 2007; Mizushima et al. 2011; Sueyoshi et al. 2012), pervaporation separation (Yoshikawa et al. 1992a, b, 1999), and selective separation of CO₂ (Yoshikawa et al. 2000).

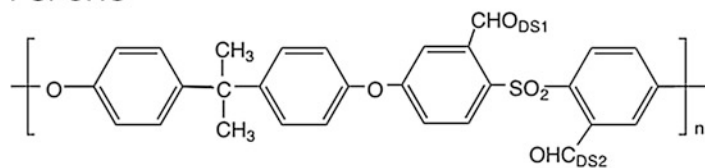
In membrane separation, both flux and permselectivity are important factors. The enhancement of permselectivity would be relatively easily attained by application of molecular

imprinting so that molecular recognition sites, which specifically incorporate target substrate into the membrane, can be introduced into a given membrane. However, the enhancement of flux without a concurrent reduction in permselectivity is perceived to be an unsolved problem or an unsolvable problem in membrane separation. In other words, flux and permselectivity often show a trade-off relationship. Membranes with high surface area and high porosity would be expected to break such a trade-off relationship between flux and permselectivity. Nanofiber membranes are expected to simultaneously give both high flux and high permselectivity. To this end, nanofiber membranes with molecular recognition sites, which are called molecularly imprinted nanofiber membranes, were fabricated by simultaneously applying an alternative molecular imprinting and an electrospray deposition (Sueyoshi et al. 2010; Yoshikawa et al. 2007). Those studies revealed that molecularly imprinted nanofiber membranes gave high flux without a concurrent reduction in permselectivity. A breakthrough in membrane separation was attained; in other words, membrane morphology in the form of molecularly imprinted nanofiber fabric was one of the suitable membrane forms to solve a trade-off relationship in membrane

Imprinted Polysulfone-Aldehyde Derivatized Nanofiber Membranes,

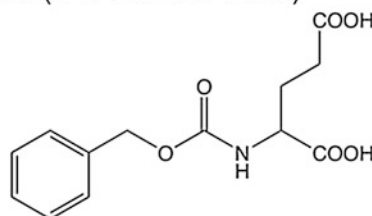
Fig. 1 Chemical structures of polysulfone with aldehyde group (PSf-CHO) and print molecule (Z-D-Glu or Z-L-Glu) (Cited from Sueyoshi et al. 2012 with permission. Copyright 2012 Elsevier Inc)

PSf-CHO



	DS
PSf-CHO-05	0.50
PSf-CHO-10	1.00
DS = DS1 + DS2	

Print Molecule (Z-D-Glu or Z-L-Glu)

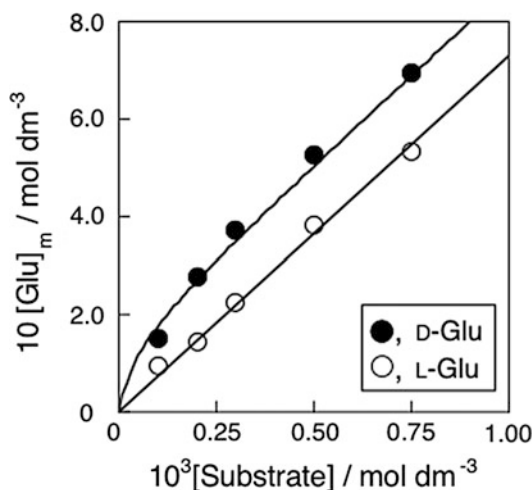
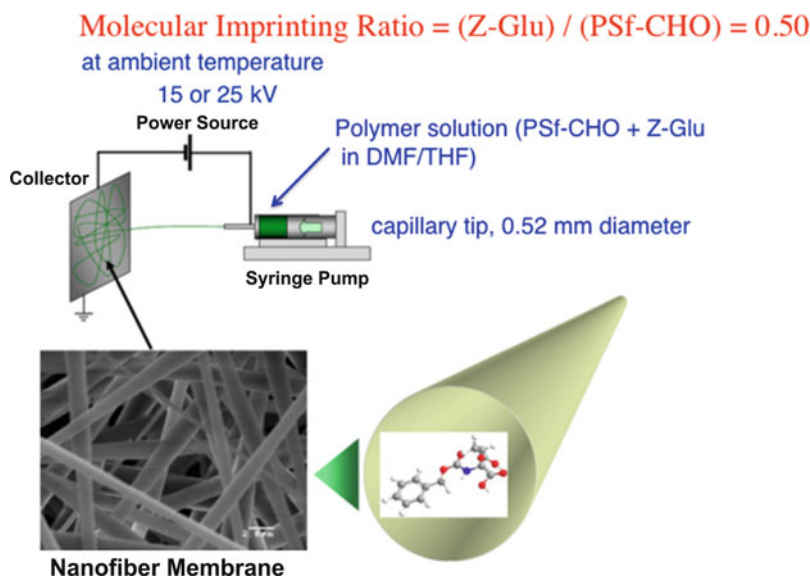


separation. Molecularly imprinted nanofiber membranes and usual molecularly imprinted membranes were fabricated from polysulfone with aldehyde group (PSf-CHO) and print molecules, and their membrane performances, such as adsorption selectivity, permselectivity, and flux, were studied (Sueyoshi et al. 2012).

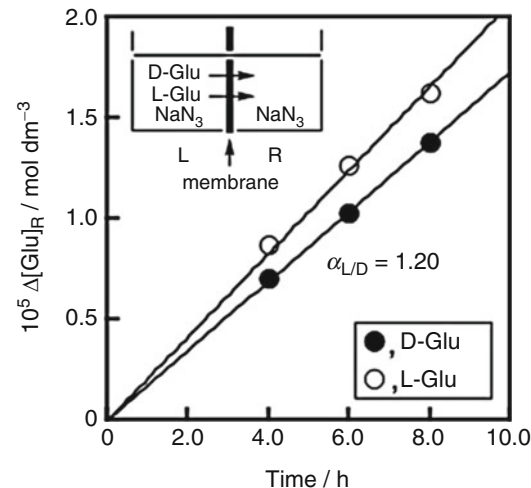
PSf-CHO with degree of substitution of 0.50 and 1.00 were adopted as candidate materials, and the derivative of D- or L-glutamic acid was applied as a print molecule to obtain molecularly imprinted nanofiber membranes and usual molecularly imprinted membranes for optical resolution (Figs. 1 and 2).

Imprinted Polysulfone-Aldehyde Derivatized Nanofiber Membranes, Fig. 2

Schematic illustration for the fabrication of molecularly imprinted nanofiber membranes, where PSf-CHO and Z-Glu were simultaneously electrospayed



Imprinted Polysulfone-Aldehyde Derivatized Nanofiber Membranes, Fig. 3 Adsorption isotherm of D-Glu and L-Glu in the nanofiber membrane molecularly imprinted by Z-D-Glu. (PSf-CHO-10 was adopted as a candidate material) (Cited from Sueyoshi et al. 2012 with permission. Copyright 2012 Elsevier Inc)



Imprinted Polysulfone-Aldehyde Derivatized Nanofiber Membranes, Fig. 4 Time-transport curves of racemic Glus through the nanofiber membrane molecularly imprinted by Z-D-Glu (PSf-CHO-10 was adopted as a candidate material) (Cited from Sueyoshi et al. 2012 with permission. Copyright 2012 Elsevier Inc)

Imprinted Polysulfone-Aldehyde Derivatized Nanofiber Membranes, Table 1 Results of chiral separation with molecularly imprinted nanofiber (MINFM's) and molecularly imprinted (MIPM's) membranes

Mmembrane	Z-D-Glu imprinted membrane			Z-L-Glu imprinted membrane		
	$\alpha_{L/D}$	u^0		$\alpha_{D/L}$	u^0	
MINFM-10 ^a	1.24	1.15×10^{-9}	(28)	1.20	1.67×10^{-9}	(41)
MIPM-10 ^a	1.20	4.20×10^{-11}	(~1)	1.20	4.10×10^{-11}	(1)
MINFM-05 ^b	1.12	7.00×10^{-9}	(231)	1.20	2.20×10^{-9}	(72)
MIPM-05 ^b	1.25	6.64×10^{-11}	(2.2)	1.16	3.05×10^{-11}	(1)

^aFigures in parentheses are the relative values; the U Value for MIPM-10 imprinted by Z-L-Glu being set as unity

^bFigures in parentheses are the relative values; the U Value for MIPM-05 imprinted by Z-L-Glu being set as unity

^c $U = (-J/C)/(d\mu/dx) [\{ (\text{mol cm cm}^{-2} \text{ h}^{-1})/(\text{mol cm}^{-3}) \} / (\text{J mol}^{-1} \text{ cm}^{-1}) = \text{mol cm cm}^{-2} \text{ J}^{-1} \text{ h}^{-1}]$.

(Cited from ref. Sueyoshi et al. 2012 with permission. Copyright 2012 Elsevier Inc.)

The membranes molecularly imprinted by Z-D-Glu incorporated the D-isomer of glutamic acid (Glu) in preference to the corresponding L-isomer and vice versa. In other words, the membrane imprinted by the L-isomer selectively adsorbed the L-isomer.

Figure 3 shows the adsorption isotherms of D-Glu and L-Glu for the Z-D-Glu molecularly imprinted nanofiber membrane as an example of adsorption isotherms. The adsorption isotherm of D-Glu, which was preferentially adsorbed in the membrane, shows a dual adsorption isotherm. It consists of nonspecific adsorption and specific adsorption on the specific recognition site, which was constructed by the presence of a print molecule during the membrane preparation process. Contrary to this, L-Glu, which was nonspecifically adsorbed in the membrane, gives a straight line passing through the origin.

Time-transport curves of racemic Glu through the D-isomer molecularly imprinted nanofiber membrane are shown in Fig. 4. As often observed, the transport of the enantiomer preferentially incorporated into the membrane was retarded by a relatively strong interaction between the enantiomer and the membrane. As a result, the antipode was selectively transported. Such discrepancy between adsorption selectivity and permselectivity is often observed in chiral separation.

Table 1 summarizes membrane performances for two types of molecularly imprinted membrane. As can be seen, the fluxes through the molecularly imprinted nanofiber membranes gave one to two orders of magnitude higher than those of usual molecularly imprinted membranes without depression of permselectivity.

As proved in the previous studies (Sueyoshi et al. 2010; Yoshikawa et al. 2007), the present study revealed that molecularly imprinted nanofiber membranes gave high flux without depression of permselectivity. The emergence of molecularly imprinted nanofiber membrane would solve a trade-off relationship in membrane separation (Yoshikawa et al. 2011).

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Imprinting

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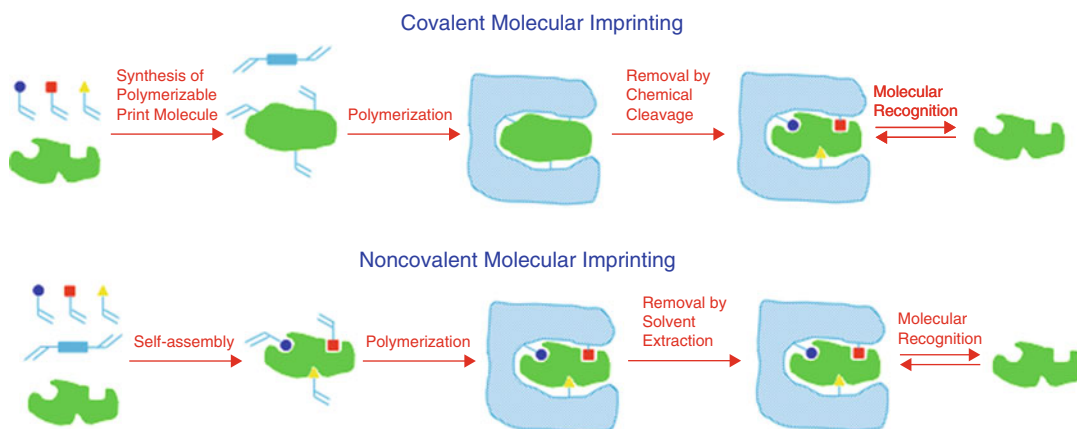
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Imprinting, which is often called “molecular imprinting,” is a facile way to introduce molecular recognition sites into polymeric membranes (materials) (Sellergren 2001; Komiyama et al. 2003; Alexander et al. 2006). In other words, the molecular memory, such as a shape of the target molecule and an alignment of the functional moieties to interact with those in target

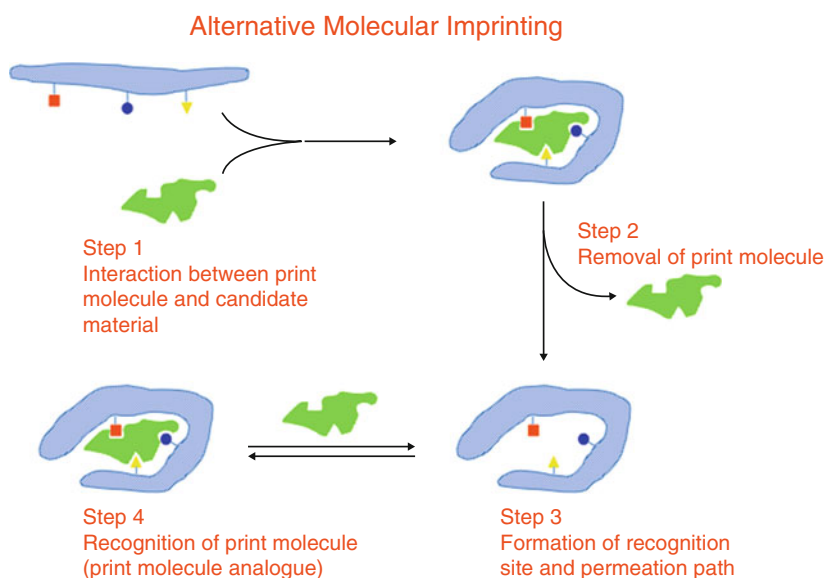
molecule, is memorized in the polymeric membranes (materials) for the recognition or separation of target molecule from others during the formation of polymeric membranes (materials).

Such molecularly imprinted materials are prepared by adopting two ways; one is “molecular imprinting,” the other “alternative molecular imprinting.” The former is a pioneering method to prepare polymeric materials with molecular recognition sites from functional monomer, crosslinker, and print molecule (template) (Wulff and Sarhan 1972; Arshady and Mosbach 1981); the molecular imprinting is further divided into two methods, covalent molecular imprinting (Wulff and Sarhan 1972) and non-covalent molecular imprinting (Arshady and Mosbach 1981) as schematically shown in Fig. 1. The latter is an alternative way to obtain polymeric membranes bearing molecular recognition sites directly from candidate polymeric materials and print molecule (Yoshikawa et al. 1995, 2011). The scheme of the alternative molecular imprinting is shown in Fig. 2. In Step 1, the polymeric material, which is a candidate material to construct molecular recognition sites, is interacted with a print molecule by specific interaction before and during the formation process of molecular recognition materials so that molecular memory can be introduced into the polymeric materials. In Step 2, the print molecule is extracted from the molecularly imprinted materials. When the molecularly imprinted material thus constructed is in contact with the print molecule or print molecule analogue, the molecular recognition sites preferentially interact with them or incorporate them into the molecular recognition sites (Step 3 and Step 4). Contrary to the pioneering molecular imprinting method, molecular recognition sites are formed at the same time as the molecularly imprinted materials are prepared from polymer solution or polymer melt. In other words, any polymeric materials, such as synthetic polymers, oligopeptide derivatives, derivatives of natural polymer, and natural polymers, can be directly converted into molecular recognition material by applying the alternative molecular imprinting (Yoshikawa 2001).



Imprinting, Fig. 1 Schemes of the covalent and non-covalent molecular imprinting (Cited from Yoshikawa et al. 2011 with permission. Copyright 2012 Elsevier Inc.)

Imprinting, Fig. 2 Scheme of the alternative molecular imprinting (Cited from Yoshikawa et al. 2011 with permission. Copyright 2012 Elsevier Inc.)



The similar approach was proposed by Michaels et al. in 1962 (Michaels et al. 1962). This study is the first report on the alternative molecular imprinting and the first application of molecularly imprinted polymeric membranes to membrane separation. Michaels' paper is the commemorable paper in molecular imprinting and membrane separation. In addition to this, molecularly imprinted polymeric membranes prepared by non-covalent molecular imprinting was reported in 1990 (Piletskii et al. 1990).

Since then, various molecularly imprinted membranes were studied by adopting non-covalent molecular imprinting. A wet phase inversion process was applied to an alternative molecular imprinting to prepare asymmetric membranes (Trotta et al. 2002).

As described above, applying molecular imprinting, such as conventional molecular imprinting or alternative molecular imprinting, molecular recognition sites are easily introduced into polymeric membranes (Ulbricht 2004). From

this, it is easy to enhance permselectivity of a given membrane by applying those molecular imprinting techniques. The enhancement of flux without a reduction in permselectivity is indispensable so that molecularly imprinted membranes can be applicable to industries.

Molecularly imprinted membranes with a higher surface area and a higher porosity are required to give higher flux and permselectivity. Electrospun nanofiber membranes with molecular recognition sites is a suitable or the best membrane morphology to attain high flux and high permselectivity. Possibility of the enhancement of flux without a concurrent reduction in permselectivity was proved by molecularly imprinted nanofiber membranes, which were fabricated by simultaneously applying an electrospray deposition and an alternative molecular imprinting (Yoshikawa et al. 2011).

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Industrial/Tannery Wastewater Treatment Using Membrane Bioreactors

► Membrane Bioreactors for Treatment of Tannery Effluents

Inert Membrane

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The term inert membrane denotes that no change in chemical reaction occurs due to contact between the membrane material and the surrounding constituents. A reaction occurring between constituents A and B to form C and D can be used as an example:



If the membrane is catalytically inactive with respect to the reaction, the term inert membrane is used to describe the membrane. The presence of a catalyst, deemed not to be part of the membrane material, may yield a change in reaction 1, and the integration of such a combination of membrane and catalyst is referred to as an inert membrane reactor (IMR). The term inert membrane is therefore commonly used in connection with membrane reactors (Koros et al. 1996) to distinguish the membrane properties from those of a catalytic membrane, the latter being catalytically active. In such reactors, the inert membrane may be used for

selectively separating reaction products from the reaction for which the catalyst serves to activate. Alternatively, the inert membrane may be employed as a distributor of reactants to ensure controlled delivery to the catalytic reaction site. Classification of a membrane as inert may also depend on the operation conditions and surface properties since the actual catalytic activity depends on parameters such as temperature, surface area, and surrounding chemical composition. Thus the same membrane may, or may not, be an inert membrane depending on the conditions under which it is operated.

The interactions between an inert membrane and its surroundings typically involve surface adsorption/desorption reactions, which may be followed by other reactions necessary for transport of matter within the membrane. For example, in the case of dense polymeric membranes, incorporation of the permeant gas molecule is required on the feed side, while the reverse process is required on the permeate side (Mulder 1996). Dense inorganic membranes, in addition, require transformation of the adsorbed molecule to atomic (in the case of metal membranes (Ward and Dao 1999)) or ionic and electronic (in the case of ceramic membranes (Sirman 2006) species at the feed side, which are then able to diffuse through the bulk membrane phase. At the permeate side, the recombination of species to the same molecular form as on the feed side takes place before desorption to the gas phase. To enhance the transformation of adsorbed gas molecules to diffusing species within the membrane and, thus, contribute to higher fluxes, catalytic surface properties are usually required. Nevertheless, such membranes which although they incorporate catalytic surface reactions, they are regarded as inert membranes since the reaction is present solely as a means of sustaining transport of the gas molecule from one membrane side to the other. Another example is inert membranes for liquid separation applications, where surface hydrophilicity and hydrophobicity may completely determine the membrane transport properties. The term inert membrane is rarely used for conventional membrane separation processes; however, one may find the term inert membrane used in such phrases as “chemically

inert membrane” or “bio-inert membrane.” These expressions refer to a specific property of the membrane such as chemical stability or compatibility in the case of chemical inertness or biological inactivity in the case of bio-inertness. In these cases the term inert membrane has a somewhat different meaning than that related to the IMRs.

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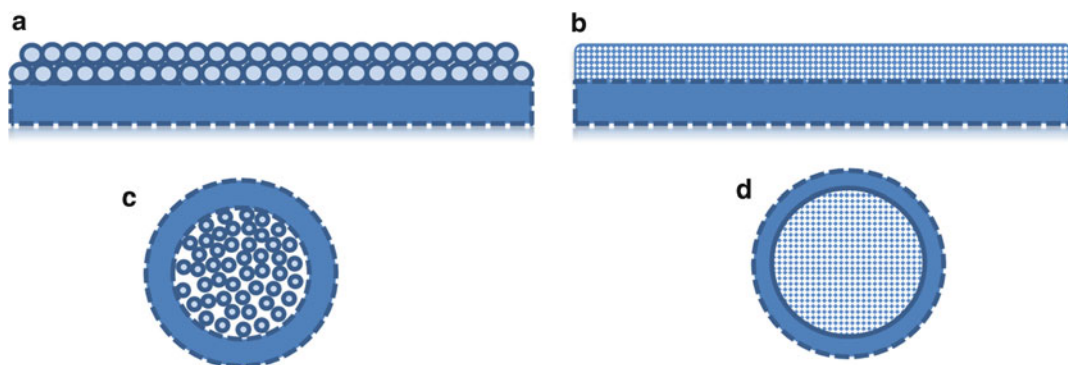
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Inert Membrane Reactors

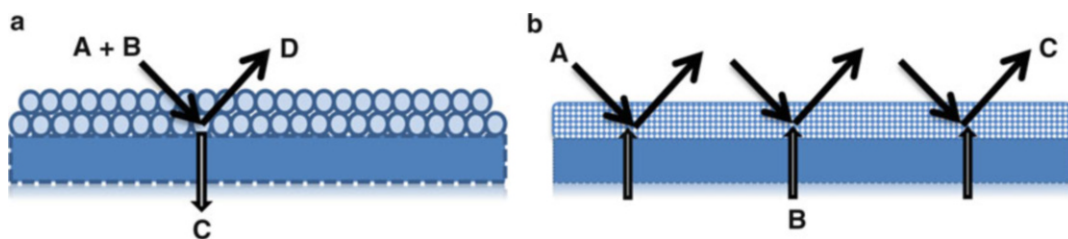
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A membrane, defined as a barrier between two phases through which transport of one or several species occurs, can be made from virtually any solid or liquid material or combinations of both. Membranes are commonly divided into inorganic, polymeric, hybrid inorganic and polymeric, or as dual phase consisting of a solid phase and a liquid phase. Furthermore, the membrane may either be dense or porous with a continuous network of pores.

A *membrane reactor* (MR) is a device for simultaneously carrying out a reaction and membrane-based separation in the same physical enclosure (Koros et al. 1996). In an *inert membrane reactor* (IMR), the *inert membrane* (*link*) and the catalyst in the form of a separate solid or



Inert Membrane Reactors, Fig. 1 Inert membrane (a) with solid catalyst, (b) with liquid containing the catalyst, (c) encapsulating solid catalyst, (d) encapsulating liquid containing the catalyst



Inert Membrane Reactors, Fig. 2 (a) Membrane extractor operation, (b) membrane distributor operation

a liquid phase are contained in the reactor (Fontananova and Drioli 2010; Julbe et al. 2001; Coronas and Santamaria 1999). Figure 1 illustrates different catalyst and inert membrane combinations in an IMR. Due to the separation of membrane and catalyst in the IMR, the membrane-based process and catalytic reactions occur in sequence. This decoupling of the processes can be advantageous with respect to operation and replacement of membrane and/or catalyst compared to MRs where the membrane serves as both catalyst and membrane. The two main functions of the membrane applied in IMRs are as an extractor or a distributor (Julbe et al. 2001; Dalmon 1997) (see Fig. 2). As an extractor, the inert membrane selectively separates a reaction product or intermediate product. The advantage may be higher conversion (equilibrium-limited reactions) or/and higher selectivity (e.g., via extraction of an intermediate that would otherwise lead to subsequent unwanted

reactions). Extraction of hydrogen from hydrocarbon dehydrogenation, reforming, or water gas shift reactions, employing hydrogen selective membranes in combination with packed or fluidized catalyst beds, has been widely studied (Sanchez Marcano and Tsotsis 2002). Dehydrogenation and reforming are typically equilibrium-limited endothermic reactions, and membrane reactor applications may benefit from the use of lower operating temperature and/or higher pressure without sacrificing yield. Esterification is yet another example of catalyzed equilibrium-limited reactions where water extraction by an inert membrane is used to increase yield (Van der Bruggen 2010). As a distributor, the inert membrane delivers the reactant in a controlled manner to the catalyzed reaction taking place in the reactor compartment (Julbe et al. 2001). The typical aim is to enhance selectivity through careful addition and temperature control of exothermic oxidation and hydrogenation reactions. Some common

examples are IMR with packed catalyst bed for oxidative coupling of methane to C₂, or oxidative dehydrogenation of hydrocarbons, by addition of oxygen and hydrogenation of alkenes by hydrogen addition. For some oxidation reactions employing IMRs, the separation of the bulk of the reactants by the membrane wall lowers the explosion potential (Coronas and Santamaria 1999).

As most membrane materials are inert, the incorporation of many different types into IMRs has been studied. Cheap polymeric membranes are advantageous with respect to capital cost, high packing density, and simple sealing technology in modules. However, their low operating temperature, typically less than 100 °C, and limited chemical stability narrow the range of applications. More expensive inorganic membranes enable high temperature operation, but since stability and transport properties are usually very temperature dependent, the different inorganic membranes have a limited window of operation. Several decades of research have shown that a number of challenges still exist with respect to high temperature applications, and commercial use of IMRs is still a future prospect. To aid reaching this future prospect, mathematical modeling and simulation is required to develop IMR design and provide an understanding of the optimal operating conditions.

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Inhibition Coefficient (IC)

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In *membrane technology*, the inhibition coefficient (*IC*) refers to a coefficient indicating quantitatively the reduction of permeability (or, equivalently, reduction of permeance or flux) of a permeating species because of one or more inhibiting species (see the entry “► [Inhibition to Permeation](#)” for definition of inhibition). The most general definition of inhibition coefficient can be provided as follows:

$$[\text{Flux}]_i^{\text{Inhib}} = (1 - IC_i) \times [\text{Flux}]_i^{\text{Clean}} \quad (1)$$

Equation 1 simply states that the flux in the presence of inhibition (indicated by the superscript “*Inhib*”) is equal to the clean (i.e., inhibition-free) flux reduced by a certain factor whose value depends on the inhibition degree. According to this definition, *IC_i* approaches the unity value (flux tending to zero) for maximum inhibition, whereas it approaches zero for minimum inhibition (flux equal to clean flux). If the clean permeation flux of the generic species *i* in mixture can be described by Eq. 2:

$$[\text{Flux}]_i^{\text{Clean}} = \frac{Pe_i^{\text{Clean}}}{\delta} \times [\text{Driving Force}]_i \quad (2)$$

and, at the same time, the surface coverage of the inhibiting species is sufficiently low to fulfill the hypotheses leading to Henry’s law, then *IC* can be

defined for the species i as reported in Eqs. 3 and 4 (Caravella et al. 2010b):

$$[\text{Flux}]_i^{\text{Inhib}} = (1 - IC_i) \times \frac{Pe_i^{\text{Clean}}}{\delta} \times [\text{Driving Force}]_i \quad (3)$$

$$[\text{Flux}]_i^{\text{Inhib}} = \frac{Pe_i^{\text{Inhib}}}{\delta} \times [\text{Driving Force}]_i \quad (4)$$

where the permeability reduction is explicitly recognized as:

$$Pe_i^{\text{Inhib}} = (1 - IC) \times Pe_i^{\text{Clean}} \quad (5)$$

For hydrogen permeation through Pd-based membranes, Eq. 2 becomes Eq. 6:

$$[\text{Flux}]_{\text{H}_2}^{\text{Clean}} = A \frac{Pe_{\text{H}_2}^{\text{Clean}}}{\delta} [(P_{\text{H}_2}^{\text{Feed}})^n - (P_{\text{H}_2}^{\text{Perm}})^n] \quad (6)$$

where $P_{\text{H}_2}^{\text{Feed}}$ [Pa] and $P_{\text{H}_2}^{\text{Perm}}$ [Pa] are the hydrogen partial pressures in feed and permeate side and δ [m] the membrane thickness. In Eq. 6, the characteristic driving force is expressed by the difference of partial pressure to the power of n , which is an empirical exponent whose value represents the macroscopic effect of all the mechanisms governing the hydrogen permeation process without inhibiting species (Caravella et al. 2010a; Flanagan and Wang 2010).

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Inhibition of Hydrogen Permeation Through Pd-Based Membranes by CO

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Synonyms

CO inhibition to Pd-based membrane

For the general concept of inhibition, see the entry “Inhibition of Permeation.” Concerning the more specific case of inhibition of hydrogen permeation through Pd-based membranes by CO – which is of crucial importance for PEM-FC applications requiring a CO content in mixture lower than 10 ppm (*Fuel Cell Handbook*, 2004) – the CO adsorption on Pd-based surface does not involve thermal dissociation and, thus, is completely reversible (Conrad et al. 1974). Therefore, properly speaking, this kind of adsorption is sometimes referred to as physical adsorption or physisorption (Conrad et al. 1974; Davies and Lambert 1981; Prigge et al. 1982; Ortega et al. 1982), different from the chemical adsorption (or chemisorption), which involves, on the contrary, a chemical bond between species and surface. This characteristics cause inhibition to decrease with increasing temperature, as adsorption and desorption are faster at higher temperatures.

With the hypotheses of validity of Henry’s law for CO (i.e., sufficiently low CO surface coverage), the hydrogen permeation flux through Pd-based membranes can be written as reported in Eqs. 1 and 2:

$$\begin{aligned} J_{\text{H}_2}^{\text{Inhib}} &= (1 - IC_{\text{H}_2, n}) \times \frac{Pe_{\text{H}_2, n}^{\text{Clean}}}{\delta} \\ &\times [(P_{\text{H}_2}^{\text{Feed}})^n - (P_{\text{H}_2}^{\text{Perm}})^n] \\ &= \frac{Pe_{\text{H}_2, n}^{\text{Inhib}}}{\delta} [(P_{\text{H}_2}^{\text{Feed}})^n - (P_{\text{H}_2}^{\text{Perm}})^n] \end{aligned} \quad (1)$$

$$Pe_{H_2,n}^{\text{Inhib}} = (1 - IC_{H_2,n})Pe_{H_2,n}^{\text{Clean}} \quad (2)$$

where $IC_{H_2,n}$ [-] is the inhibition coefficient, Pe is membrane permeability, and n is an empirical exponent whose value is an indication of the interactions among the mechanisms controlling the hydrogen permeation. The subscript n indicates that both membrane permeability and inhibition coefficient depend on the value of n .

In the particular case in which the original Sieverts' law can be applied, the pressure exponent n is equal to 0.5 (indicated by the superscript "Siev"), and Eq. 1 becomes (Caravella et al. 2010):

$$J_{H_2}^{\text{Inhib}} = (1 - IC_{H_2,\text{Siev}}) \times \frac{Pe_{H_2,\text{Siev}}^{\text{Clean}}}{\delta} \times \left[\sqrt{P_{H_2}^{\text{Feed}}} - \sqrt{P_{H_2}^{\text{Perm}}} \right] \quad (3)$$

In all the reported expressions, the values of the partial pressures must be those adjacent to the membrane surface. In the absence of appreciable external mass transfer resistance (concentration polarization), these values coincide with the bulk values. However, the presence of inhibition always includes a certain level of concentration polarization, as the inhibiting species do not permeate through membrane, generating in this way an additional resistance not only on membrane surface but also in the fluid phase of the feed side.

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Inhibition to Permeation

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In physical chemistry and chemical engineering, inhibition mostly refers to a phenomenon for which one or more species prevents other species from reaching active sites of a surface by a competitive reversible site occupation. The reversibility of this phenomenon makes it different from poisoning, which affects irreversibly the considered surface.

Historically speaking, inhibition has firstly regarded the activity reduction of catalysts. However, with the development of membrane technology, the concept of "catalytic surface" has become wider, this more generally referring also to surfaces interacting with chemical species in processes of adsorption/desorption and solubilization/desolubilization from membrane surface to membrane bulk and vice versa (i.e., not necessarily involving net chemical reactions).

If the driving force promoting permeation through membrane can be represented by the pressure difference of a generic species i , the transmembrane flow rate F_i (mol s⁻¹) and flux J_i (mol m⁻² s⁻¹) are expressed by Eq. 1 in absence of inhibition (indicated by the superscript "Clean"):

$$\begin{aligned} F_i^{\text{Clean}} &= A_{\text{Mem}}^{\text{Clean}} J_i^{\text{Clean}} \\ &= A_{\text{Mem}}^{\text{Clean}} \frac{Pe_i^{\text{Clean}}}{\delta} [P_i^{\text{Feed}} - P_i^{\text{Perm}}] \end{aligned} \quad (1)$$

where P_i^{Feed} (Pa) and P_i^{Perm} (Pa) are the partial pressure of hydrogen in feed and permeate side,

δ (m) is the membrane thickness, and A_{Mem} (m^2) is the membrane area. In general, for membranes as well as for catalysts, the reduction of active sites directly corresponds to a reduction of the effective catalytic surface. From this point of view, the intrinsic membrane permeability Pe_i^{Clean} ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$) – i.e., the permeability evaluated in clean (inhibition-free) conditions – is not affected by inhibiting species.

However, as it is extremely difficult to know the exact amount of surface reduction due to inhibition (and, thus, not available to permeation), in some cases the inhibition effect can be dealt with by considering a reduction of permeability (Eq. 2) rather than a reduction of surface (Eq. 3).

$$\begin{aligned} F_i^{\text{Inhib}} &= A_{\text{Mem}}^{\text{Clean}} J_i^{\text{Inhib}} \\ &= A_{\text{Mem}}^{\text{Clean}} \frac{Pe_i^{\text{Inhib}}}{\delta} [P_i^{\text{Feed}} - P_i^{\text{Perm}}] \quad (2) \end{aligned}$$

$$\begin{aligned} F_i^{\text{Inhib}} &= A_{\text{Mem}}^{\text{Inhib}} J_i^{\text{Clean}} \\ &= A_{\text{Mem}}^{\text{Inhib}} \frac{Pe_i^{\text{Clean}}}{\delta} [P_i^{\text{Feed}} - P_i^{\text{Perm}}] \quad (3) \end{aligned}$$

The expressions 2 and 3 can be used under the hypothesis of low surface coverage of inhibiting species (i.e., within Henry's law hypotheses) (Caravella et al. 2010). For higher values of surface coverage due to inhibiting species, the driving force is gradually less suitable to be described by a simple function of feed and permeate partial pressure, it involving, on the contrary, more complex expressions of the partial pressure of all the species in mixture. The overall form of these expressions cannot be easily generalized, as they strongly depend on the functionality of the adsorption/desorption mechanism on the surface as well as on that of the diffusion mechanism through membrane.

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Inorganic Acids Recovery by Nanofiltration

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Nanofiltration (NF) is a type of membrane which functions in a similar way to reverse osmosis, but is generally used to retain divalent ions and allow monovalent ions to pass through. Nanofiltration has been used to recover the metal or acid value from the mining and metal finishing industries. In recent years, nanofiltration has become an emerging technology for the recovery of strong acids – inorganic (mineral) acidic solutions such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), nitric acid (HNO_3), and hydrofluoric acid (HF). These acids are commonly used in the winning, electroplating, acidic pickling, and etching process. The acid strength of the solutions can be varied up to 33 wt.% H_2SO_4 , 35 wt.% H_3PO_4 , and 10 wt.% HNO_3 .

Nanofiltration is increasingly applied to separate the metal ions and at the same time recycling the acidic solutions back to the plating bath. The performance of nanofiltration in acid recovery is complicated by their exclusion mechanism of nanofiltration which includes adsorption, size exclusion, coulombic interactions, and dielectric exclusion. Due to the monovalent of proton ($1+$) and its smaller ionic radius (hydrated oxonium ion) than water, nanofiltration has relatively lower acid (proton) rejection. However, the transport of acids across the membrane also depends on their counterions. The solution pH will affect the membrane surface zeta potential and acid recovery performance. For example, if the isoelectric point of the membrane is 4, then above pH 4, the membrane will be negatively charged. Under this pH, sulfate ion will be repelled and less proton permeation is expected in order to maintain the Donnan Equilibrium in the feed stream. On the other hand, at low pH, the membrane will have net positive charge. Permeation of multivalence ions (SO_4^{2-}) will be favorable; thus proton permeation will be enhanced to maintain electroneutrality.

Inorganic Acids Recovery by Nanofiltration, Table 1 Comparative rejection data^a

Acid	RO(%)	NF(%)
H ₂ SO ₄	~98	0–10
HCl	~90	~0

^aPerformance depends on the feed concentration

Another important concerning factor in acid/metal separation is the chemical speciation problem as weak acids form neutral species under low acidic conditions. Separation of neutral acid using NF therefore will solely depend on size exclusion. Besides, the permeate flux is strongly influenced by acid viscosity and osmotic pressure. The permeate flux decreased as the acid concentration increased due to the acid viscosity.

Membrane stability is always a concerning issue for their application in acid recovery. Commercial polymeric nanofiltration membranes are typically stable in the pH range of 2–12. Membranes of interest include CK (pH 2–8)/DK (pH 2–10) (Osmonics), SeIRO MPF-34 (Koch, pH range 0–14), NF45 (Dow, pH 3–10), PVD-1 (Hydranautics), and NF-PES-10 (Nadir) (Soldenhoff et al. 2005). The report from Cleaner Production Germany shows that nanofiltration is suitable to be used for the treatment of sulfuric pickling solutions at plant trial scale. Metal concentrations of 80 g/l were achieved in the concentrate (99 % rejection), and sulfuric acid was able to pass through the membrane at a flux of 30 l/m².h to give filtrate (permeate) amounting to 250 g/l. In this process, up to 99 % of the acid residue and the water can be returned to the pickling process (Cleaner Production Germany 2004). The general rejection data of acid using RO and NF membranes are generalized in Table 1. It shows that NF is relatively poor in retaining acid compared to the RO membrane which makes it very interesting in metal/acid separation.

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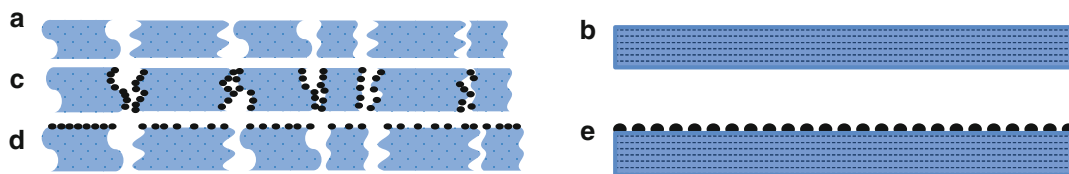
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Inorganic Catalytic Membrane

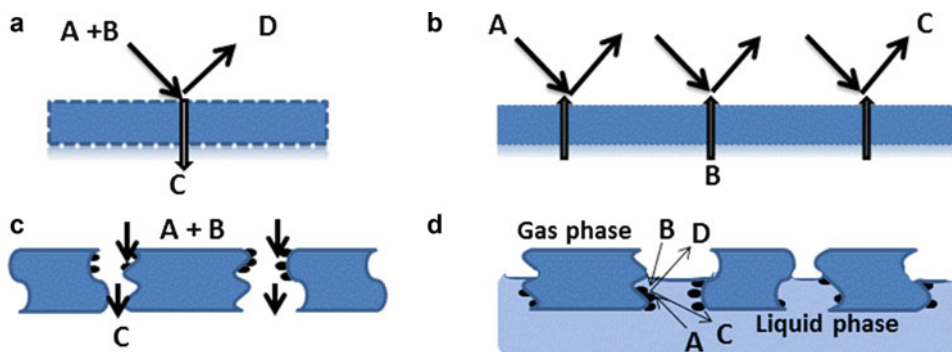
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An inorganic catalytic membrane is an inorganic membrane that is catalytically active. Inorganic membranes are made from metals, ceramics, glass, and carbon and may be porous or dense. The term inorganic catalytic membrane is typically meant in the context of membrane reactors where yield is enhanced by combining a membrane separation and a catalyzed chemical reaction. Inorganic catalytic membranes can either be composed of an inherently catalytically active material or an inert membrane structure to which a catalytically active phase is added on the outer surface or inside pores (Specchia et al. 2006), see Fig. 1. In the latter case, integration of catalyst material and inorganic membrane structure is carried out by common deposition and impregnation methods such as wet (electro)chemical deposition, chemical vapor deposition, or physical vapor deposition. Since the membrane is catalytic, reaction and separation occur in parallel a feature which distinguishes it from the sequential processes of inert membrane reactors where the inert membrane and catalyst material are separated. The function of the membrane may serve as extractor, distributor, or contactor depending on application (Dalmon 1997) (see Fig. 2) and the reaction mechanism can be (electro)catalytic, photo-catalytic, or bio-catalytic. The many different concepts and envisaged applications are described comprehensively in various text books and scientific papers (Gryaznov et al. 2006; Sanchez Marcano and Tsotsis 2002; Caro 2010; Fontananova and Drioli 2010).



Inorganic Catalytic Membrane, Fig. 1 Inherently catalytic (a) porous, (b) dense membrane. Inert membrane with catalyst deposited (c) inside pores, on outer surface of (d) porous, and (e) dense membrane



Inorganic Catalytic Membrane, Fig. 2 Inorganic catalytic membrane in (a) extractor operation, (b) distributor operation, (c) flow-through contactor operation, (d) liquid–gas contactor operation

Inorganic catalytic membranes can operate at higher temperatures than their polymeric counterpart, which opens a broader window of operation as high temperature is also required for many important reactions which are limited by low yield in traditional reactors. The assembling of inorganic catalytic membranes in membrane modules may, however, give too low a catalytic surface area and limited conversion and therefore render operation less cost efficient compared to more conventional reactors. To mitigate this problem, additional catalyst can be added to the reactor volume. In order to increase efficiency, some current development activities are aimed at manufacturing inorganic thin capillary, multichannel, and hollow fiber membranes with high surface area/volume ratio.

The dual operational nature of inorganic catalytic membranes is particularly challenging since both membrane and catalytic properties must work satisfactory. Commonly encountered issues related to degradation processes such as

adsorption, poisoning, clogging, and fouling are all critical and membrane lifetime may suffer when trying to achieve the optimal trade-off between membrane and catalyst properties. Common examples of applications include hydrocarbon dehydrogenation, hydrocarbon reforming, and hydrogenation of alkenes for which hydrogen selective inorganic catalytic membranes can be used (Sanchez Marciano and Tsotsis 2002). Combination of endothermic (e.g., water splitting to produce hydrogen) and exothermic (e.g., partial oxidation of methane) reactions for integrated mass and heat transport has been demonstrated by using catalytically active oxygen permeable membranes (Caro 2010). By feeding oxygen in a controlled manner, partial oxidation of hydrocarbons to form synthesis gas, oxidative coupling of methane, and oxidative dehydrogenation reactions have been demonstrated using dense and porous inorganic catalytic membranes (Sanchez Marciano and Tsotsis 2002; Coronas and Santamaria 1999; Sammells et al. 2006). When

porous inorganic catalytic membranes are used as flow-through contactors, a forced close spatial contact between reactants and catalyst can give improved conversion efficiency compared to reactions in catalyst powder beds (Westermann and Melin 2009). Additionally, higher selectivity may be achieved due to the short and well-defined contact time between reactants and membrane catalyst. Yet in another contactor mode, the porous inorganic catalytic membrane provides a defined catalytic region for reaction and controls transport of reactants from both sides of the membrane. For example, in liquid–gas catalytic contactors, both hydrogenation and oxidative reactions have been demonstrated.

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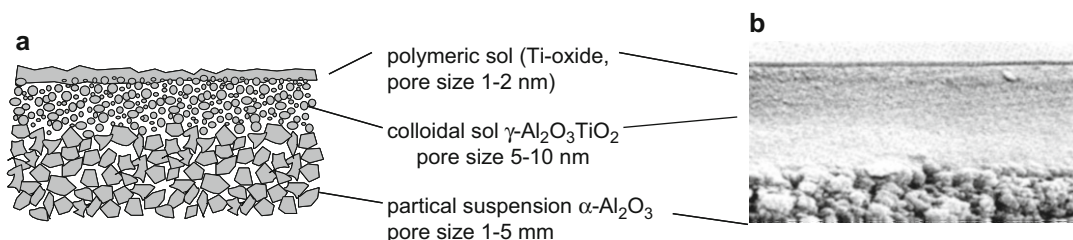
Inorganic Composite Membrane Preparation

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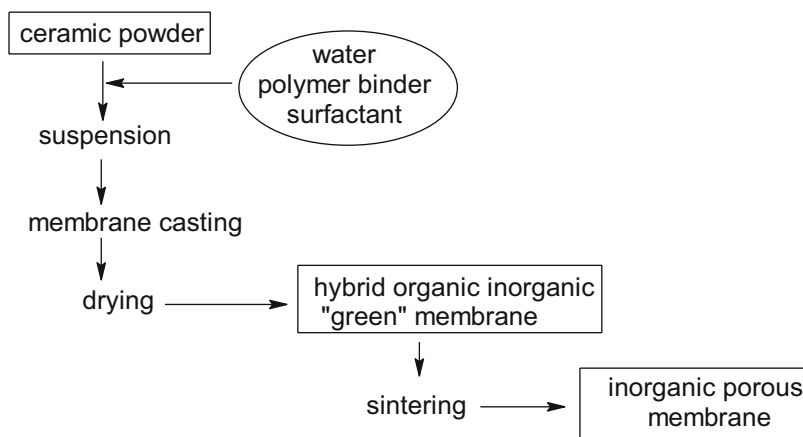
Ceramic membranes to be used in micro-, ultra-, and nanofiltration as well as in pervaporation and gas separation are also prepared as multiple-layer composite structures (Burggraaf et al. 1996). A typical three-layer structure of an ultra- or nanofiltration membrane is shown schematically in Fig. 1a and as a scanning electron micrograph in Fig. 1b indicating the materials and the pore size of the different layers. The first support layer is generally prepared from a suspension of Al_2O_3 powder using an organic polymer such as cellulose or polyvinyl alcohol as a binder and to increase the viscosity of the suspension. The suspension can be processed by slip casting or extrusion into flat sheets, hollow fibers, or tubes forming the so-called green structure which is dried and converted into the final membrane by sintering at ca. 1500 °C resulting in a porous structure of $\alpha\text{-Al}_2\text{O}_3$ with an average pore diameter of 5 or more μm and an overall porosity of about 35 %. The process is indicated in Fig. 2. A second layer prepared by a so-called sol–gel process is deposited on the support layer by dip coating or filtration. The sol used in this process consists of colloidal particles as indicated in the schematic drawing of Fig. 2. The material used for the preparation of the second layer is usually $\gamma\text{-Al}_2\text{O}_3$ or TiO_2 . The pore size of this layer is in the range of 5–10 nm. Thus, the two-layer membrane can be used for micro- and ultrafiltration applications. For the separation of lower molecular weight components in nanofiltration and pervaporation a third layer is deposited. This



Inorganic Composite Membrane Preparation, Fig. 1 (a) Schematic drawing illustrating the structure of a three-layer inorganic composite membrane, (b) Scanning electron micrograph of a three-layer ceramic membrane

Inorganic Composite Membrane Preparation, Fig. 2

Porous inorganic membrane preparation scheme based on slip-casting of a ceramic powder and sintering at 1500–1800 °C



layer is also prepared by the sol–gel process. However, the sol contains an inorganic polymer as indicated in Fig. 2 which forms a polymer gel consisting of a three-dimensional network. As material for the inorganic structure TiO_2 , ZrO_2 , or SiO_2 is often used (Liebau 1988).

A suspension is a dispersion of solid particles in a liquid; a sol is the suspension of colloidal particles or polymers. The main difference between suspension and sol is the size of the dispersed particles. Suspensions are prepared from a fine powder of aluminum oxide with an average particle diameter of 5 – 10 μm . The dispersion is mixed with an organic polymer such as polyvinyl alcohol or a cellulose derivative and poured in a mold or extruded in the desired shape as a flat sheet, tube, or capillary; dried; and sintered at 1500 – 1800 °C. The process scheme is shown in Fig. 2.

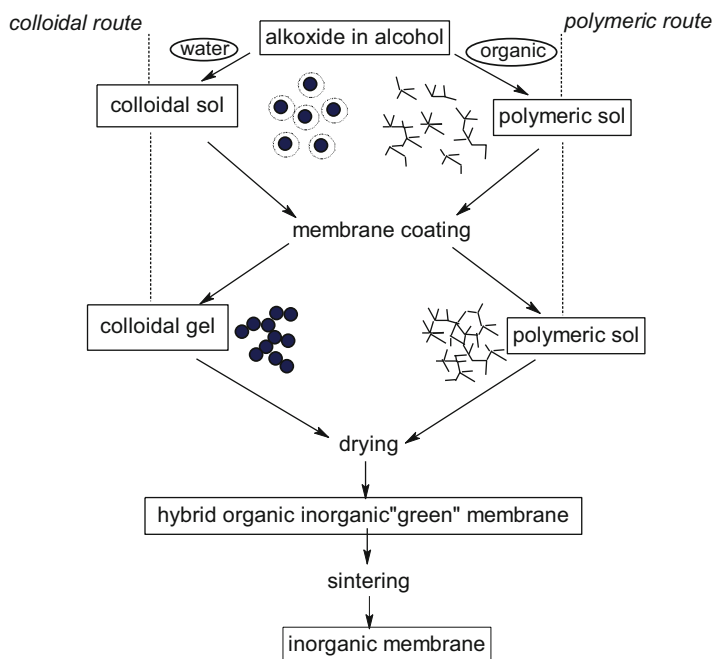
One surface of the support structure is then coated again with a suspension of finer particles,

dried, and sintered again. Sometimes, more than one coating is applied to obtain the desired pore size at the surface of the membrane. The process preparing a multilayer membrane by suspensions of different particle sizes is referred to as slip coating. With the slip-coating process membranes with pore sizes down to 20 nm to be used in micro- ultrafiltration can be made. To obtain membranes with smaller pores a sol–gel process is applied and a colloidal or polymeric gel is used which is prepared by controlled hydrolysis of a metal alkoxide to a hydroxide. The process can follow two different process paths. One path is referred to as the colloidal and the other the polymeric process path. Both pathways are illustrated in Fig. 3.

In the colloidal process path a metal oxide such as aluminum oxide is dissolved in alcohol and then hydrolyzed and precipitated by addition of excess water at elevated temperature to form a stable colloidal solution. The solution is cooled

Inorganic Composite Membrane Preparation,

Fig. 3 Schematic diagram illustrating the colloidal and polymeric route of the sol–gel process used in the preparation of composite inorganic membranes



to form a gel, which is then coated on an appropriate support and sintered at ca. 800 °C. The average pore diameter obtained in the colloidal sol–gel process is in the range of 2–5 nm.

The overall process consists of three steps:

- Metal alkoxide formation: $\text{Al}_2\text{O}_3 + \text{alcohol} \rightarrow \text{Al(OR)}_3$
- Precipitation: $\text{Al(OR)}_3 + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 \rightarrow \gamma - \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Böhmite)
- Coating and sintering: $\gamma - \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} \rightarrow \gamma - \text{Al}_2\text{O}_3$

In the polymeric sol–gel process the metal alkoxide is only partially hydrolyzed in an alcohol solution by a controlled addition of a minimum of water. The hydroxyl groups of the alkoxide react with each other and form an inorganic/organic polymer, which forms a clear gel that is coated on the support structure. It is dried and sintered at 500 – 800 °C and further cross-linked to form a porous structure with a pore diameter of less than 1 nm. For the polymer sol–gel process often a titanium alkoxide is used which is converted into a cross-linked inorganic polymer in three steps:

- Hydrolysis of the metal alkoxide
- Polymerization and coating
- Sintering and cross-linking

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Inorganic Fillers

- [Filler in Membranes](#)

Inorganic Fouling

- [Inorganic Scaling](#)

Inorganic Scaling

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Synonyms

Inorganic fouling

Inorganic scaling occurs in reverse osmosis (RO) applications and is caused by the retention of sparingly soluble mineral salts such as calcium carbonate, calcium sulfate, calcium phosphate, barium sulfate, magnesium salts, silica, etc. Due to water removal and concentration polarization (CP), the concentrations build up and can exceed the saturation level and cause scaling of the membrane surface. Membrane scaling has two pathways, namely, surface crystallization and bulk crystallization. For surface crystallization, CP causes the sparingly soluble salt concentration at the membrane surface to exceed the solubility limit. Consequently, the surface is gradually covered by the lateral growth of a crystal deposit that reduces the effective area for permeation. For fixed imposed flux, the local flux increases in order to compensate for loss of area, and this increases the local CP level which exacerbates the scale formation. In the other pathways, crystals form in the bulk phase when concentrations exceed saturation level due to high recovery (defined as fraction of feedwater removed as permeate). Crystals in suspension are then deposited on the membrane and eventually form a porous cake layer, which provides a hydraulic resistance. There are many membrane elements connected in series in a RO plant, and concentration builds up from the feed to the tail end. Scale formation is therefore more prevalent in the tail end elements of the plant. It is likely that both scaling mechanisms, surface and bulk, could occur simultaneously in a RO system. This is because a

crystal cake causes “cake-enhanced concentration polarization” (CECP) (see “[Irreversible Fouling Resistance](#)”), and the increased CP of the scale formers leads to precipitation on the membrane and within the cake.

There are several strategies to control scaling in membrane systems. Bulk crystallization can be mitigated by controlling the supersaturation level of the salts by limiting the maximum recovery in the RO system. The effect of CP on surface concentration can be manipulated by the ratio of flux to crossflow velocity, where lower CP is favored by modest flux and raised crossflow velocity. Most scale formers are more soluble at lower pH, so the injection of acid into the feed stream can provide some control. The exception to this is silica scaling which is more serious at lower pH and requires an increase in pH. If silica and calcium scalants are both present, it may be necessary to soften the feed by ion exchange to remove the calcium and then raise the pH. Scale formation can also be controlled by the use of antiscalant chemicals. These are proprietary materials, but include various molecular weight polycarboxylates and polyacrylates, usually dosed at a few ppm level. Care needs to be taken with antiscalant selection as some tend to promote biofouling.

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Integrated Membrane Processes for Biofuel Production

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Biofuels are important solutions to worldwide energy crisis and greenhouse effect. Their

production through chemical, physiochemical, or biochemical conversions is one of the many procedures involved in biorefinery. Due to the complexity of the conversion mechanisms and feedstocks, what are delivered in the fuel generation procedures are not highly purified fuels but a mixture of a series of organics containing the fuels in some concentration range. In fermentation process to produce liquid bioalcohols, the situation is further complicated by the existence of bacterial cells inside the yeast cultures. In this regard, integration of separation technologies to recover the biofuels, remove other components, or enhance the concentration of biofuels is indispensable to biofuel production. The separation technologies used to refine and upgrade biofuels include distillation, membrane separation, gas stripping, liquid–liquid extraction, etc. (Vane 2005). The reasons to consider membrane separation include moderate temperature, space efficiency, and easy operation.

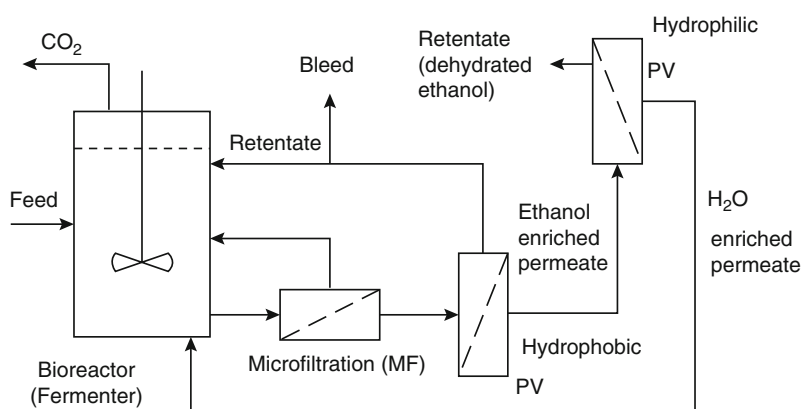
Several types of integrated processes using membrane as key units are employed in biofuel production. In bioethanol production, an integrated membrane process as illustrated in Fig. 1 is employed (Huang et al. 2008). In achieving recovery of volatile organic compounds (VOCs) containing the alcohols from the fermentation process, hydrophobic pervaporation and membrane distillation are used. There also exist in the fermentation broth some other chemicals with higher molecular weight such as phenolics, carboxylic acids, and amino acids. Various techniques for recovery or extraction of these

value-added chemicals have already been reviewed (Schugerl 2000). Other metabolites such as carbon dioxide (CO_2) and ammonia (NH_3) can be removed easily by aeration stripping. Pervaporation or membrane distillation has the dual function of rejecting the cells and preferentially removing the VOCs, simultaneously. But more often, a microfiltration membrane is used to hold back the microbes, so that the hydrophobic membrane, the more costly unit, will not be fouled. With the above separation procedures, the fermentation process can be carried out continuously and obtain improved productivity and conversion rate. The recovered VOCs (ethanol, acetone, butanol, 2-propanol) are directly reused within other processes or further separated. In principle, gas stripping or adsorption is more accurate in discriminating these VOCs (Schugerl 2000). Upon obtaining the ethanol-enriched aqueous solution, it is dehydrated by hybrid system incorporating distillation and pervaporation. Intensive dehydration by adsorption might be performed on condition that the purity is required to be very high. Similar design of integrated process can be used in biobutanol production.

The most common way to produce biodiesel is transesterification that transforms triglyceride extracted from vegetable oil, animal fats, grease, or algae into fatty acid alkyl esters (FAME) in the presence of alcohol (e.g., methanol) and a catalyst (e.g., acid, base) (Shuit and Subhash 2012). Two major membrane separation procedures are integrated in the above process. For the real-time separation of products from the feed mixture,

Integrated Membrane Processes for Biofuel Production,

Fig. 1 Integrated membrane process for bioethanol production (Adapted from Huang et al. 2008)



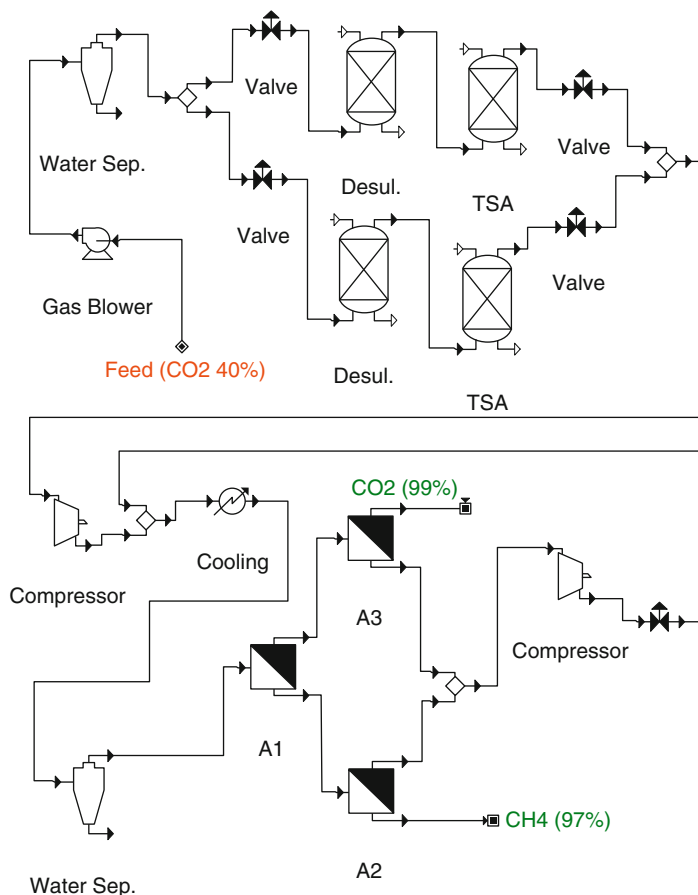
porous membrane is used to retain the oil droplet larger than the pore size while allowing the alcohol, glycerol, and biodiesel to pass through. Thereafter, glycerol is removed to obtain purified biodiesel also by using porous membrane (e.g., MF), wherein the reversed micelles binding glycerol are rejected (Wang et al. 2009). If dense membrane (e.g., pervaporation) selectively transfers glycerol that is used, one-step separation can replace the above two-step separation. Following removal of glycerol, biodiesel is further purified to remove impurities such as tri-, di-, and monoglycerides, catalyst, soap, and traces of alcohol. The removal of these impurities is essential as the presence of these impurities poses great impact

on the purity and quality of biodiesel as fuel for use in compression–ignition engines.

High-temperature gasification and anaerobic digestion are major approaches for producing biogas containing H_2 , carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), etc. The integrated process for biogas upgrading includes two parts (Shuit and Subhash 2012). The pretreatment shown in the top part removes impurities including H_2S , H_2O , other VOCs, and siloxanes mainly using adsorption and temperature swing adsorption. The treated feed is delivered to the membrane system that consists of three blocks as shown in Fig. 2. In block 1, the feed is separated into a CO_2 -enriched permeate and a CH_4 -enriched

Integrated Membrane Processes for Biofuel Production,

Fig. 2 Integrated process for upgrading biogas from anaerobic digestion (Adapted from Shao et al. 2002)



retentate. They are further enriched to 99.0 vol.% in block 2 and 97.0 vol.% in block 3, respectively.

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Integration of Membrane Separation with Biotechnology

► Membrane Biotechnology

Intermittent Feed Diafiltration

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Intermittent feed diafiltration is characterized as a batch diafiltration process in which the processed liquor is first concentrated to a predetermined volume and then diluted back

to its original volume with a diluent. This concentration–dilution sequence may be repeated several times to obtain the desired degree of separation of macrosolutes from microsolute. As a final step, an additional post-concentration may be applied to achieve the required final volume. A mathematical analysis of intermittent feed diafiltration can be found in (Wang et al. 2007).

Note that the processing scheme of intermittent feed diafiltration is basically a slight modification of the method employed by sequential dilution diafiltration (also called discontinuous diafiltration by sequential dilution).

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Intrinsic Activation Energy

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Transport phenomena and chemical reaction rates are influenced by temperature. This effect is reflected on the numerical value of the coefficient rate, which therefore depends on the variable temperature. Both for mass transfer coefficient and chemical reaction coefficient, various theoretical approaches have been suggested in order to predict and quantify their dependency on the temperature. However, these approaches have had limited success, and the effect of the temperature is generally obtained through experimental evidence. A generally accepted relationship linking kinetic coefficient and temperature is the Arrhenius' law, which is written as

$$k = k_0 \exp\left(-\frac{E}{RT}\right)$$

where k is the generic kinetic coefficient, E is the activation energy, R is the universal gas constant, and T is the absolute pressure.

Arrhenius' law is basically an empirical relationship which however has been found to reproduce with the satisfactory accuracy of experimental data and the effect of temperature. A small value of the activation energy E corresponds to a weak influence of the temperature on the kinetic constant, whereas a large value of the activation energy E is representative of kinetic constant strongly influenced by temperature. Just as a reference, for gas phase chemical reaction, the activation energy is normally high, in the range of 50–250 kJ/mol, while that for diffusion coefficient is less than 10 kJ/mol).

The classic way to estimate the activation coefficient from experimental data is to utilize a plot having $1/T$ on the x-axis and $\ln(k)$ on the y-axis. The slope of the best fitting curve passing through the experimental points will yield the value of the ratio (E/R) and consequently that of E .

Ion Beam Irradiation

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Ion beam irradiation has long been recognized as an effective method for the synthesis and modification of diverse materials, including polymers (Davenas et al. 1989; Xu et al. 1995a, b). Ion beam irradiation is the bombardment of a substance with energetic ions. When the ions penetrate through the surface of a membrane, they may eliminate the tall peaks and deep valleys, resulting in an overall reduction in surface roughness (Xu and Coleman 1997). As the ions penetrate

the membrane, they lose energy to their surroundings (membrane structure) by two main processes: interacting with target nuclei (nuclear stopping) and interacting with target electrons (electronic stopping; Lee 1999).

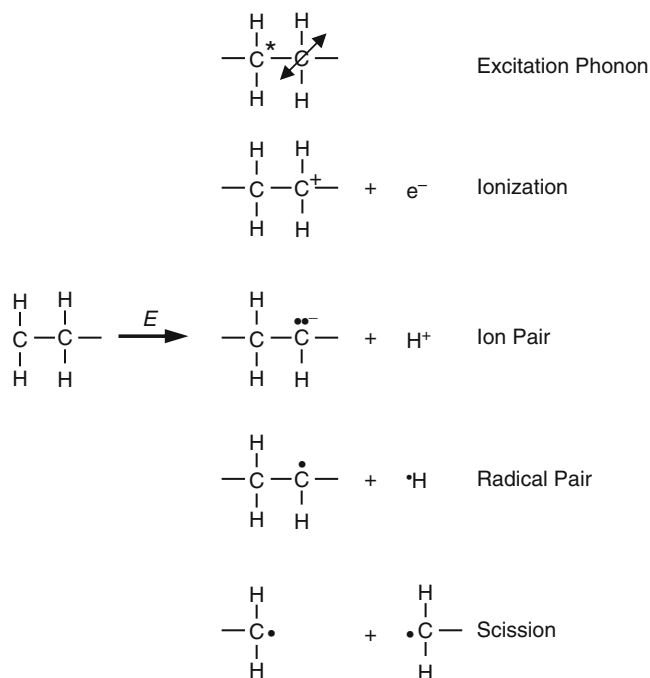
Nuclear stopping energy losses arise from collisions between energetic particles and target nuclei (Davenas et al. 1989; Lee 1999). Atomic displacement occurs when the colliding ion imparts energy greater than certain displacement threshold energy. If the energy is not great enough for displacement, the energy dissipates as atomic vibrations known as phonons. The threshold energy is the energy that a recoil requires to overcome binding forces and to move more than one atomic spacing away from its original site. The interaction of an ion with a target nucleus is treated as the scattering of two screened particles since the nuclear collision occurs between two atoms with electrons around protons and neutrons. Nuclear stopping varies with ion velocity as well as the charges of two colliding atoms, as it is derived with consideration of the momentum transfer from ion to target atom and the interatomic potential between two atoms.

Electronic stopping energy losses arise from electromagnetic interaction between the positively charged ions and the target electrons (Lee 1999). There are two mechanisms: one is called glancing collisions (inelastic scattering, distant resonant collisions with small momentum transfer), which are quite frequent, but each collision involves a small energy loss (<100 eV), and the other is called knock-on collisions (elastic scattering, close collisions with large momentum transfer), which are very infrequent, but each collision imparts a large energy to a target electron (>100 eV). Both collisions transfer energy in two ways: electronic excitation and ionization. Excitation is the process in which an electron jumps to a higher energy level, while in ionization an orbital electron is ejected from the atom.

Various gaseous molecular species are released during irradiation. The most prominent emission is hydrogen, followed by less abundant heavier

Ion Beam Irradiation,

Fig. 1 Typical consequences induced by ion irradiation, which include electronic excitation, phonons, ionization, ion pair formation, radical formation, and chain scission



molecular species, which are scission products from the pendant side groups and chain-end segments, and their reaction products (Lee 1999). Figure 1 illustrates various functional chemical entities created by irradiation. Cross-linking occurs when two free dangling ion or radical pairs on neighboring chains combine, whereas double or triple bonds are formed if two neighboring radicals in the same chain combine. It has been well established that mechanical, physical, and chemical property changes in polymers are determined by the magnitude of cross-linking and scission and that cross-linking enhances mechanical stability while scission degrades mechanical strength (Lee et al. 1996). The intensive energy deposition in polymers can lead to the following: (1) formation of volatile molecules and free radicals which leave defects in the polymer matrix, (2) creation of additional cross-linking between polymer chains, (3) formation of new chemical bonds, and (4) chemical reactions with chemical atmosphere such as oxidation (Lee 1999). These

four events can, in turn, lead to membrane microstructure alterations.

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Ion-Exchange Membrane Characterization

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Characterization of ion-exchange membranes is closely related to their preparation. The most interesting properties of ion-exchange membranes are (Spiegler 1958):

- The electrical resistance in different electrolyte solutions
- The type and density of fixed charges and their distribution in the membrane matrix
- The permselectivity of the membrane for different ions
- The transport rate of neutral components, especially water
- The mechanical and chemical stability and the swelling in different electrolyte solutions

A series of procedures and techniques are applied to determine the different membrane properties. Microscopic examination yields information on heterogeneity of the membrane structure and in case of reinforced membranes the type of reinforcement used. The electrical charge of an ion-exchange membrane can be determined qualitatively by using indicator solutions. A drop of a 0.05 % solution of methylene blue and methyl orange on a membrane sample stains a yellow

spot on top of an anion-exchange membrane and a deep blue spot on top of a cation-exchange membrane, respectively. For a quantitative characterization, more complex procedures such as the determination of the ion-exchange capacity or the electrical resistance and transport properties for different ions of the membrane are applied. Additional information can be obtained by impedance spectroscopy and chronopotentiometric measurements or from the determination of osmotic and electroosmotic water transfer. Bipolar membranes are further characterized in terms of the water dissociation capability and salt leakage under operating conditions (Strathmann et al. 1993).

Hydraulic Permeability of Ion-Exchange Membranes

Hydraulic permeability measurements provide information on the diffusive or convective transport of components through a membrane under a hydrostatic pressure driving force. In most practical applications of electrodialysis, the hydraulic permeability due to diffusion plays a minor role for the overall performance of the membrane in a given process. However, for the determination of pinholes in ion-exchange membranes will affect the performance of a membrane severely in applications with a hydrostatic pressure differences across the membrane. Pinholes can be detected quickly by placing a wet membrane sheet on a sheet of white absorbent paper. Then, a 0.2 % solution of methylene blue for an anion-exchange membrane or a 0.2 % solution of erythrosin B for a cation-exchange membrane is spread over the entire surface of the membrane. If no spots of the dye can be observed on the paper, the membrane is free of large pinholes. The hydraulic permeability of the membrane is determined at room temperature using deionized water and a hydrostatic pressure driving force in a conventional filtration cell as used in reverse osmosis or ultrafiltration experiments. The permeability can then be calculated from the volumetric flow rate.

The economics of processes using ion-exchange membranes in different applications

is determined to a large extent by the chemical stability of the membranes under process conditions. Generally, the changes in membrane properties are time and temperature dependent. Reliable information about the long-term stability of the membranes is of importance for a process design and cost calculation. For a fast evaluation, membrane samples are exposed to oxidizing agents or acids and bases and other chemical components in much higher concentration and at higher temperature than expected in practical use. Structural mechanical changes are determined by visual or microscopic investigation and standard mechanical and electrochemical tests comparing exposed with unexposed membrane samples. Since the useful life of membranes under process conditions is generally in the range of a couple of years, membrane stability tests are very time consuming. However, in many cases long-term pilot plant tests are mandatory to get a reliable estimation of the life of the membranes in practical applications.

The performance of ion-exchange membranes in the various processes is determined to a very large extent by their electrochemical properties. Therefore, a major task in characterizing ion-exchange membranes is the determination of their electrochemical properties such as the fixed charge density, the electrical resistance, the ion permselectivity, and the transport of nonionic components such as water or of other neutral molecules under operating conditions.

The Ion-Exchange Capacity of a Membrane

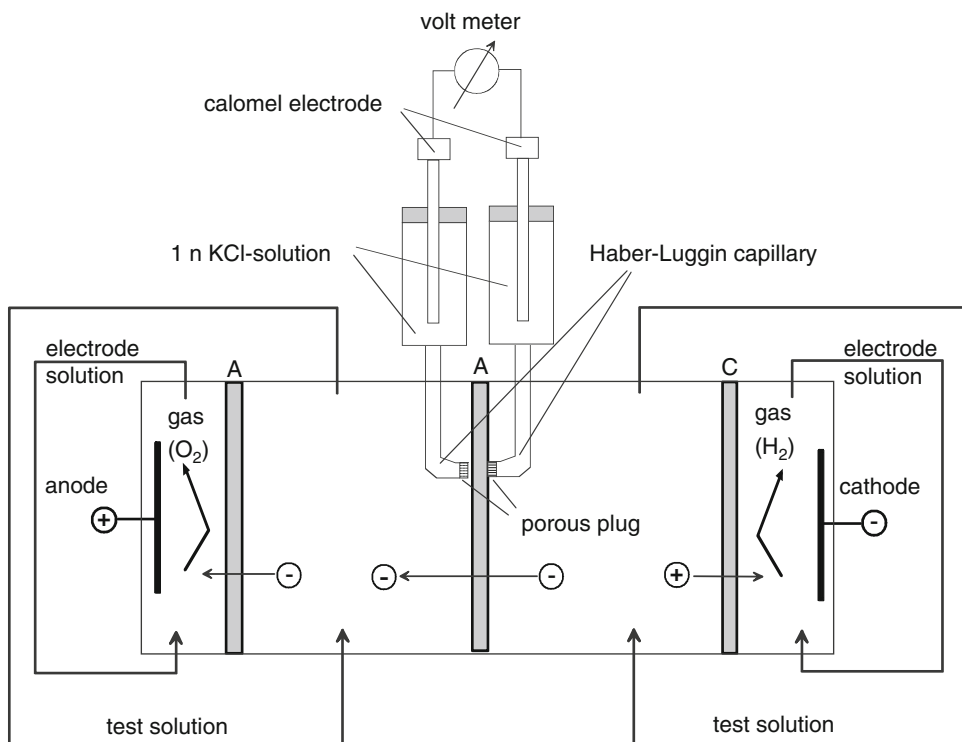
The ion-exchange capacity of membranes is a crucial parameter which affects almost all other membrane properties. It is usually expressed in milliequivalent per gram of dry membrane. Experimentally, the ion-exchange capacity of strong acidic or strong basic ion-exchange membranes is readily determined by titration with NaOH or HCl, respectively. For these tests, cation- and anion-exchange membranes are equilibrated in 1N HCl or 1N NaOH, respectively, and then rinsed free from chloride or sodium ions with deionized

water. The ion-exchange capacity of the samples is determined by back titration with 1N NaOH or 1N HCl, respectively. Weak base anion-exchange membranes are characterized by equilibration in 1N NaCl and titration with standardized 0.1N AgNO₃ solution. The samples are then dried, and the ion-exchange capacity is calculated based on the dry membrane. The accuracy of the measurement depends on the complete exchange of ions in the membrane which can take some time. The concentration of the fixed ion in commercial membranes is in the range between 1 and 3 milliequivalent per gram. The experimentally measured ion-exchange capacity of a membrane is an average value assuming that the ions are homogeneously distributed over the entire polymer matrix. In many heterogeneous membranes, such as most of the perfluorinated cation-exchange membranes, the fixed ions are clustered, and the local fixed ion concentration may be significantly higher than the average value.

Determination of the Electrical Resistance of Ion-Exchange Membranes

The electrical resistance of ion-exchange membranes is an important parameter determining to the energy consumption in electrodialysis (Strathmann et al. 2006). The specific membrane resistance is usually reported as Ω cm or Ω m. From the engineering point of view, the membrane area resistance in units of Ω cm² or Ω m² is more useful and generally given in the literature describing commercial products. The electrical resistance of a membrane is determined by the ion-exchange capacity and the mobility of the ion within the membrane matrix. The ion mobility in the membrane depends strongly on the nature of the mobile and fixed ion species. It is furthermore affected by the temperature.

The area resistance of ion-exchange membranes can be determined by direct current (DC) or alternating current (AC) measurements. In DC measurements the membrane is installed in a cell which consists of two chambers containing the test solution separated by the test membrane as indicated in Fig. 1.



Ion-Exchange Membrane Characterization, Fig. 1 Schematic drawing of a test cell for determining the resistance of ion-exchange membranes with direct current

The two electrodes used to provide the electrical potential driving force to obtain a certain current are separated by membranes from the test solution to avoid gas bubbles to disturb the measurement. As test solution a 1 or 0.5 mol/L Na_2SO_4 solution is used. The same solution is also used to rinse the electrode chambers and remove the gases produced at the electrodes. The actual potential drop in DC measurements across the membrane is determined with calomel electrodes attached to Haber-Luggin capillaries placed with their tips close to the membrane surface. The potential drop between the Haber-Luggin capillaries is measured with and without the membrane in the test cell as a function of the current density passing through the cell. The resistance is given by the slope of the current versus the voltage drop curve. To obtain the membrane resistance, the resistance of the cell without the membrane is subtracted from the resistance of the cell with the membrane.

The area resistance is given by:

$$r_{m+s} = RA_m = \frac{U}{i} \quad (1)$$

The membrane resistance is:

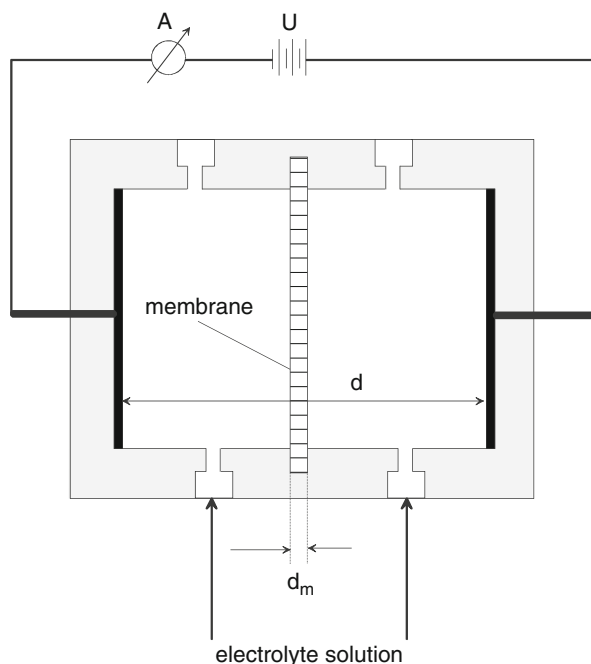
$$r_m = r_{m+s} - r_s \quad (2)$$

Here R is the resistance, A_m is the area of the membrane, U is the voltage drop measured between the Haber-Luggin capillaries and i is the current density, r_{m+s} and r_s are the area resistances of the cell with and without the membrane between the Haber-Luggin capillaries, and r_m is the area resistance of the membrane.

The determination of the membrane resistance by direct current measurements is quite accurate as long as the position of the Haber-Luggin capillaries is as close as possible to the membrane and kept identical in the test with and without the

Ion-Exchange Membrane Characterization,

Fig. 2 Schematic drawing of a test cell used for membrane resistance measurements using alternating current



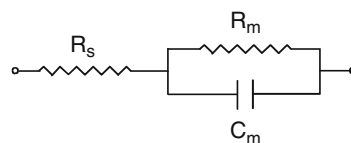
membrane. To avoid boundary layer effects, the bulk solution must be well mixed. But even if the boundary layer effects are well controlled, the direct current measurements are always connected with a transport of ions resulting in a concentration change in the electrolyte solution at the membrane surface which affects the accuracy of the measurement.

Concentration changes at the membrane surface are avoided in resistance measurements with alternating current. A typical test cell used for resistance measurements with alternating current is shown in Fig. 3. The membrane resistance is determined from resistance measurements in a cell with and without membrane. The resistance of the membrane can be calculated from the following relation:

The area resistance r_m is related to the specific resistance by:

$$r_m = \rho_{m+s}(d_m + d) - \rho_s d \quad (3)$$

Here r_m are the area resistances of the membrane, ρ_{m+s} and ρ_s are the specific resistances of the cell with and without the membrane, and d_m and d are



Ion-Exchange Membrane Characterization,

Fig. 3 Equivalent resistance-capacitance circuit for a simple membrane in an electrolyte solution neglecting electrode resistances and capacities

the thickness of the membrane and the distance between the electrodes.

The specific resistance ρ is:

$$\rho = R \frac{A_m}{d} \quad (4)$$

Here A_m is the cross-sectional area of the cell as indicated in Fig. 2 and R is the resistance measured between the electrodes.

For an accurate determination of the membrane resistance, it is important that the difference between the measurement of the cell resistance with and without a membrane is as large as possible. Since the specific resistances of the membrane and the electrolyte solution are in the same

order of magnitude and the membrane thickness d_m is small, the distance d has to be as small as possible.

Comparing the direct and alternating current membrane characterization processes often significant differences in the measured resistances of more than 50 % is often observed. The alternating current measurements give a much lower membrane resistance than the direct current measurements. This is a general finding. However, the magnitude of the difference in the results depends on the membrane structure. In very heterogeneous membranes, the difference is larger than in more homogeneous membrane structures. The reason for the different results is that in direct current measurements, the ions are physically transported through the membrane matrix, whereas in alternating current measurements, the ions are only oscillating around their locations. Assuming the structure of an ion-exchange membrane consists of a microscopic scale of a solid neutral polymer phase and electrolyte-filled pores, then the mobility of the ions in the pore liquid is high. But their transport through the membrane is hindered by the solid polymer structure which acts as a bottleneck between pores. This type of structure is typical for fluorocarbon membranes. In alternating current measurements, the transport of the ions on a very small scale, i.e., in a pore, is measured. In direct current measurements, the transport of the ions is measured on a macroscopic scale which includes also the passage through a bottleneck between electrolyte-filled pores. The direct current and alternating current difference is treated in detail in the literature (Zabolotsky and Nikonenko 1993).

A rather simple and reliable method of measuring resistances is based on impedance spectroscopy. The difference between the alternating current resistance measurements and the impedance spectroscopy is that in the first case, the frequency of the alternating current is kept constant, while in impedance spectroscopy the frequency of the alternating current is changed, and the response to the changing frequency is determined by a spectrometer.

Ion-exchange membranes display a variety of electrical properties that suggest that they can be modeled as a combination of electrical analog components. For example, an applied potential can produce a current flow through the membrane, and this is indication that the membrane has a finite resistance. In addition, the charged groups at the membrane/solution interface provide sites for the redistribution of charges at the membrane surface when the potential is changed. This charge redistribution is similar to that observed for a capacitor in which a potential change produces a change in the net charges. The electrolyte solutions and the electrodes on both sides of the membrane also have a certain resistance. The properties of the ion-exchange membrane, the solution, and the electrodes can be described electrically by an equivalent circuit as indicated in Fig. 3, where C_m and R_m are the membrane capacitance and resistance, respectively, and R_s is the resistance of electrodes and the electrolyte solution.

To determine membrane resistances by impedance spectroscopy, the entire system, i.e., the membrane, the electrolyte, and the electrodes, is treated as a "black box." An alternating sinusoidal voltage of a given frequency and amplitude is applied to the system. The resulting current is measured, and then the phase shift compared to the input signal is determined. The procedure is repeated at different frequencies (see entry "Impedance Spectroscopy, Membrane Characterization by).

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Ion-Exchange Membrane for Fuel Cells

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Low-temperature fuel cells can be equipped with a proton or anion exchange membrane in alternative to liquid electrolytes (Aricò et al. 2001). The core of a polymer electrolyte fuel cell (PEMFC) is the ion exchange membrane. The electrodes (anode and cathode) are in intimate contact with the membrane faces. The membrane determines the fuel cell resistance and the fuel permeation rate, and it influences the reaction rate. It is well known that the use of non-noble metal catalysts is possible in the presence of alkaline electrolytes. Protons conducting electrolytes have been preferred to alkaline electrolytes for several decades for practical reasons, e.g., to avoid carbonation. The standard electrolyte membrane is usually a perfluorosulfonic acid membrane such as Nafion. Most of the electrolytes alternative to Nafion both proton conducting and alkaline type, e.g., hydrocarbon type, are significantly cheaper, and in some cases, they are also characterized by smaller hydrogen and methanol crossover. However, lifetime characteristics similar to those shown by Nafion-type membranes in fuel cells have not yet been demonstrated for the alternative membranes. Concerning with the conductivity, only recently, membrane alternative to Nafion type have shown similar levels of performance. One critical aspect is related to the fact that the presence of water is a requirement of low-temperature PEMFCs and DMFCs for the occurrence of the electrochemical reactions and to promote ion conductivity (water-assisted conductivity mechanism). High ionic conductivities are often associated to the presence of large water uptake by the membrane, but this property often causes poor mechanical characteristics such as large swelling and relevant crossover (especially methanol). Phosphoric acid-doped polybenzimidazole membranes use a

Grotthus mechanism of proton transport and do not require water (Wang et al. 1995). These membranes operate at about 180–200 °C. Whereas composite perfluorosulfonic acid membranes or sulfonated hydrocarbon including inorganic fillers such as silica rely on the water-assisted mechanism, they can operate up to 145 °C, under particular conditions (3 bar abs pressure), due to the enhanced water retention of the filler (Aricò et al. 2003).

Composite recast Nafion® membranes containing inorganic fillers have been employed in high temperature (~150 °C) direct alcohol (Aricò et al. 1998) and H₂-air fuel cells (Watanabe et al. 1996). These composite membranes were originally developed for reduced humidification operation in polymer electrolyte fuel cells (Watanabe et al. 1996) due to the enhanced water retention inside the membrane by the effect of the inorganic filler (Aricò et al. 1998). A further advantage of composite membranes relies in the barrier effect given by the inorganic filler for methanol crossover (Ren et al. 1996).

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Ion-Exchange Membrane Preparation

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Definition

An ion exchange membrane is a membrane through which ions permeate selectively between two aqueous phases by diffusion or electromigration. Ion exchange membranes are prepared with polymeric materials, inorganic salts, or composite materials. This entry describes the preparation of ion exchange membranes mostly based on polymeric materials. Like other membranes, an ion exchange membrane should have a high flux and a high selectivity, often characterized by electrochemical properties representing transport of ions. The desired properties of ion exchange membranes are (i) high ionic conductivity, (ii) high transport number, (iii) good mechanical stability, and (iv) high chemical and thermal stability. Ion exchange membranes are prepared by binding ion exchange functional groups on the polymer backbone with or without supporting matrix. Therefore, the main components of ion exchange membrane fabrication are polymer material for a base membrane, functional groups, and supporting matrix.

Base Membrane

The polymers used for ion exchange membranes are polyethylene, polystyrene, poly(vinylimidazole), poly(acrylonitrile), polyphosphazene, polysulfone, poly(ether ether ketone), poly(phenylene oxide), etc. (Sata 2004). The polymer is selected based on possibility of functionalization, polymer processability, chemical and mechanical stability, and compatibility with supporting matrix.

A polymeric base membrane is formed as a sheet by casting a polymer solution or polymerization of monomers appropriately. Polymerization is carried out by heat and/or UV radiation with initiators. Various fabrication processes have been developed such as sandwich method, latex method, block copolymerization, paste method, and graft polymerization (Tanaka 2007). The thickness of a base membrane is about 100–200 μm , thinner membranes being developed for low electric resistance. When an ion exchange membrane is used under harsh conditions such as extreme pH or high electron activity, hydrogen atom in the polymer backbone is easily attacked, causing degradation of the membrane. Common approaches to eliminate the α -hydrogen are uses of fluorinated polymers, aromatic chain polymers, and sulfone group.

Functionalization

The base membrane is to be functionalized by sulfonation for a cation exchange membrane (CEM) or by amination for an anion exchange membrane (AEM). Frequently used sulfonating reagents are sulfuric acid, chlorosulfuric acid, a mixture of sulfuric acid and chlorosulfuric acid, dioxane- SO_3 complex, and pyridine- SO_3 complex. Also a base membrane is functionalized with aminating agents such as trimethylamine (TMA), triethylamine (TEA), 1,4-diazabicyclo[2.2.2]octane (DABCO), *N,N,N,N*-tetramethylethylenediamine (TMEDA), and tris(2,4,6-trimethoxyphenyl)-phosphine (TTMPP) to make an AEM (Toshikatsu et al. 2004). Typical functional groups on polymer backbones for CEMs are SO_3H , $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, phenolic OH, $\text{C}(\text{CF}_2)_3\text{OH}$, and $-\text{CF}_2\text{SO}_2\text{NHR}$, and those for AEMs are $-\text{NH}_2$, $-\text{NH}$, $-\text{aniline}(\text{NH}_2)$, $-\text{N}(\text{CH}_3)_3\text{OH}$, $-\text{S}(\text{CH}_3)_2\text{OH}$, and $-\text{P}(\text{CH}_3)_3\text{OH}$. Some functional groups are attached by graft methods with the help of plasma or γ -ray radiation. An amphoteric membrane contains both cationic and anionic functional groups in the polymer backbone which are interacting with counter ions differently depending on the environmental pH.

A mosaic membrane is prepared by blending cation exchange polymer and anion exchange polymer. Also ion exchange membranes can be prepared by polymerization of a monomer that contains a cationic or an anionic moiety with neutral polymer (Strathmann 2004) called pre-functionalization. Monovalent selective ion exchange membranes are prepared by coating regular ion exchange membranes with highly cross-linked polymer material or oppositely charged ion exchange layer.

Reinforcement

Often a polymeric base membrane is hydrophobic without ion exchange capacity. When the base membrane turns to an ion exchange membrane, the membrane becomes hydrophilic by ionic solvation as ion exchange capacity increases. The hydrophilicity leads to high conductivity and adverse effects such as swelling and mechanical weakness of the membrane. To improve the stability of the hydrophilic ion exchange membrane, reinforcing material is to be introduced. Chemically inert powder (e.g., PVC, SiO₂, TiO₂), nonwoven or woven fabrics (e.g., PVC, bacterial cellulose, electrospun fiber), and porous sheets (e.g., PE, PP, PTFE) are employed as reinforcing material. This type of membranes is called hybrid or composite membranes. Inorganic particles such as SiO₂ rather increase the hydrophilicity while passage of non-charged compounds is blocked effectively. Another way to strengthen the membrane is cross-linking the polymer chain, since a linear polymer chain is flexible and readily absorbs solvent including water. A frequently used cross-linking agent is divinylbenzene. In some cases polymer chains are cross-linked by condensation reaction, and functional groups are involved in the reaction at a high temperature. Generally electrochemical properties, i.e., ion exchange capacity and conductivity, should be compromised with chemical and mechanical stability in the membrane preparation with reinforcing materials.

Heterogeneous Membrane

Heterogeneous membranes are fabricated by binding ion exchange particles and cast on a plate or film. Ion exchange resin beads are ground, by a ball mill or a high speed blender, in preparing fine particles to be uniformly mixed with binder in solvent. A heterogeneous ion exchange membrane is thicker (500–1,000 μm) than a homogeneous ion exchange membrane and advantageous in mechanical strength, but exhibiting a high electric resistance.

Bipolar Membrane

A bipolar membrane is a sandwich-type ion exchange membrane made with a sheet of cation exchange membrane and that of anion exchange membrane. Practically a bipolar membrane is prepared by applying an anion exchange layer on a cation exchange membrane, or vice versa. When a bipolar membrane is prepared with prefabricated ion exchange membranes, the contacting sides should be slightly roughened to apply binder, so that the interface resistance may be minimized. Since the membrane is used for water dissociation under an electric field at an overvoltage, catalyst for the water dissociation reaction should be placed in the interface between the cation exchange layer and the anion exchange layer. Typical catalysts are soluble metal ions or insoluble metal oxides.

Porous Membrane

Usually ion exchange membranes are considered as nonporous since their pores are not controlled and ions pass through ion channel with minimized convective flow. The diameter of ion channel is known as 1–5 nm which is filled with pendant-type functional groups in an aqueous phase. While nonporous ion exchange membranes are dominantly utilized, porous ion exchange membranes are investigated for limited applications where a high flux transport is required at a slightly lower

selectivity. Such porous ion exchange membranes are prepared by phase inversion to control nanometer size pores, followed by functionalization. Alternatively pre-functionalized polymer dissolved in solvent is cast and dried in air or nonsolvent (e.g., water) to form pores in the membrane.

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hydrocarbon or fluorinated hydrocarbon polymers which carry positively or negatively charged ions fixed to the polymer structure (Xu 2005; Bergsma and Kruissink 1961; Molau 1981). The type and the concentration of the fixed ions in a membrane structure determine permselectivity and the electrical resistance of a membrane, while the chemical stability and the mechanical properties of the membrane are determined mainly by the matrix polymer. There are three types of ion-exchange membranes:

- Cation-exchange membranes which contain fixed negatively charged ions and which have a selective permeability for cations
- Anion-exchange membranes which contain fixed positively charged ions and which have a selective permeability for anions
- Bipolar membranes which consist of a cation- and an anion-exchange membrane laminated together

Ion-Exchange Membranes

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Ion-exchange membranes. Most of today's ion-exchange membranes used in commercially relevant processes are 0.2–1 mm thin sheet of

The ions often used as fixed charges in cation-exchange membranes are $-\text{SO}_3^-$ and $-\text{COO}^-$.

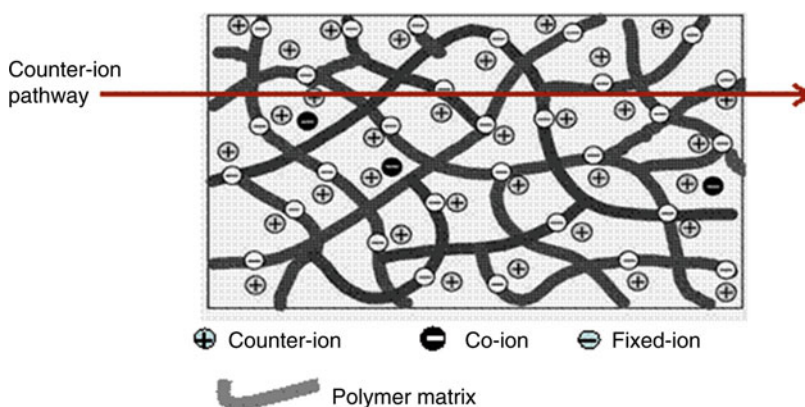
Fixed charges used in anion-exchange membranes are $-\text{N}^+ \text{H R}_2$ and $-\text{N}^+ \text{R}_3$.

The structure of a cation-exchange membrane is illustrated in Fig. 1 which shows the polymer matrix with the fixed negative ions and the mobile counterions as well as their pathway through the membrane.

The most desired properties for ion-exchange membranes are:

Ion-Exchange Membranes,

Fig. 1 Schematic drawing illustrating the structure of a cation-exchange membrane showing fixed negative ions and mobile positive counterions in the polymer matrix



- High permselectivity – an ion-exchange membrane should be highly permeable for counterions, but should be impermeable to co-ions.
- Low electrical resistance – the permeability of an ion-exchange membrane for the counterions under the driving force of an electrical potential gradient should be as high as possible.
- Good mechanical and form stability – the membrane should be mechanically strong and should have a low degree of swelling or shrinking in transition from dilute to concentrated ion solutions.
- High chemical stability – the membrane should be stable over the entire pH range from 1 to 14 and in the presence of oxidizing agents.

For the practical preparation of ion-exchange membranes, two rather different procedures are used. The first procedure results in a homogeneous ion-exchange membrane structure and is closely related to the preparation of ion-exchange resins. Homogeneous ion-exchange membranes are produced by either a polymerization of monomers that carry anionic or cationic moieties or by introducing these moieties into a polymer which may be in an appropriate solution or a solid preformed film. The second widely used ion-exchange membrane preparation technique which leads to a rather heterogeneous structure is based on mixing an ion-exchange resin powder with a binder polymer, such as polyvinylchloride or polyethylene, and extruding the mixture as a film at a temperature close to the melting point of the polymer.

A cation-exchange membrane with exceptional good chemical and thermal stability which is widely used in the electrolytic chlorine-alkaline production and as polymer electrolyte in low-temperature fuel cell consists of a polyfluorocarbon material. This membrane is often referred to as “Nafion[®] membrane” which is the trade name of DuPont. There are several more ion-exchange membranes with special properties commercially available such as the bipolar membrane which is composed of an anion- and a cation-exchange layer laminated together (Simons 1993).

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Ion-Exchange Membranes in Chlor-Alkali Process

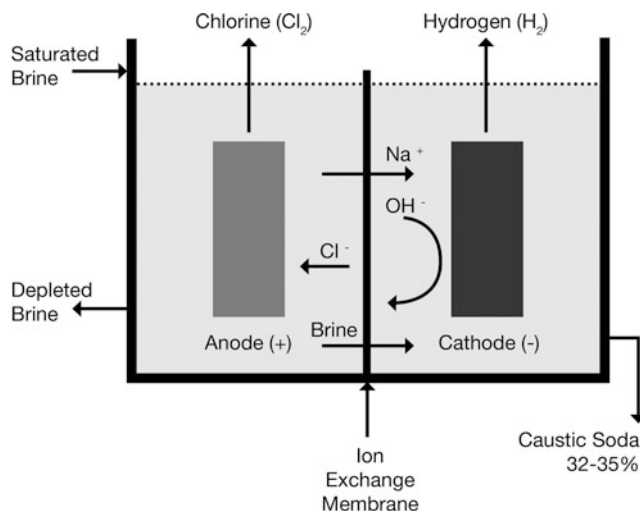
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Ion-exchange membranes in chlor-alkali process (also called ion exchange membranes in chlor-alkali membrane cell process) are the synthetic membranes employed to produce chlorine (Cl_2) and alkali, sodium hydroxide (NaOH) or potassium hydroxide (KOH) by electrolysis of a salt solution. These membranes are permeable to either positively or negatively charged ions in aqueous solution used in the chlor-alkali industry. The membranes that are selectively permeable to positively charged ions are usually named cation-exchange membranes (CEM), and membranes selectively permeable for negatively charged ions are called anion membranes (AEM). The selectivity occurs due to high concentration of immobile (fixed) ions within the membrane body.

Cation membranes have negatively charged fixed ions usually sulfonic or carboxyl groups chemically bound with the membrane's matrix. Their charge is neutralized by positively charged ions (counterions). An anion membrane would have positively charged fixed ions, usually quaternary ammonium groups, and negatively charged counterions. Fixed ions and counterions are connected by ionic bounds in a dry membrane. In the swollen membrane, this bond would be dissociated. Therefore, the counterion is mobile

Ion-Exchange Membranes in Chlor-Alkali Process, Fig. 1 Membrane cell process in chlor-alkali industry



and can be replaced by another ion. Hence the membrane would be permeable to ions with the charge sign opposite to the charge of the fixed ion. This unique property makes ion-exchange membrane applications very attractive for chemical industry, because it allows for the removal, addition, substitution, depletion, or concentration of ions in process solutions (Baker 2000; Nunes and Peinemann 2001).

The chlor-alkali (also called “chlorine-caustic”) industry is one of the largest electrochemical technologies in the world. It is an energy-intensive process and is the second largest consumer of electricity (2400 billion kWh) among electrolytic industries. The chlor-alkali industry produces chlorine and caustic solution (sodium or potassium hydroxide) simultaneously by means of decomposition of a saturated sodium chloride solution often called “brine.” Along with the chlorine and the caustic solution, hydrogen is produced. There are three basic processes for the electrolytic production of chlorine. These three processes are the diaphragm cell process, the mercury cell process, and the membrane cell process. The distinguishing difference between the technologies relies in the manner by which the anolyte and the catholyte streams are prevented from mixing with each other. Separation is achieved in a diaphragm cell by a separator and in a membrane cell by an ion-exchange membrane. In mercury cells, the cathode itself acts as

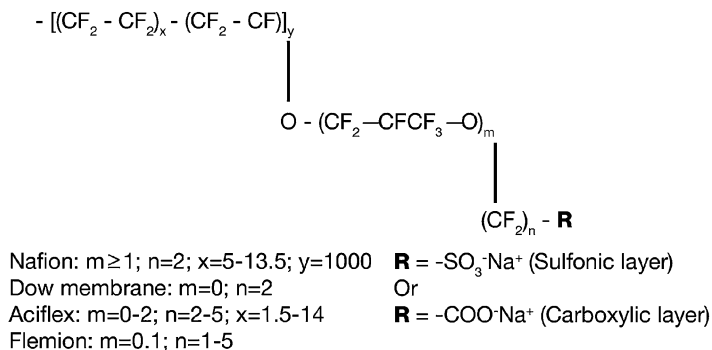
a separator by forming an alloy of sodium and mercury (sodium amalgam) which is subsequently reacted with water to form sodium hydroxide and hydrogen in a separate reactor (O’Brien et al. 2005).

The membrane cell technology has several advantages compared to the other processes: high energy efficient, high purity of caustic, and low environmental impact; the membrane process does not use highly toxic materials such as mercury and asbestos. Disadvantages of the membrane process are that the caustic soda produced may need to be evaporated to increase concentration and, for some applications, the chlorine gas produced needs to be processed to remove oxygen. Furthermore, the brine entering a membrane cell must be of a very high purity, which often requires costly, additional purification steps prior to electrolysis. Nowadays, the membrane cell process is the most used in the world, and in Europe, complete conversion to the membrane technology is expected in the next years due to the mandatory deadline (2020) to phase out the mercury cells (Euro Chlor 2011; de Bastos Vidal 2013).

In a membrane cell, an ion-exchange membrane separates the anode and cathode compartments (Fig. 1). The separator is generally a bilayer membrane made of perfluorocarboxylic and perfluorosulfonic acid-based films, intercalated between the anode and the cathode. The saturated brine is fed to the anode compartment where

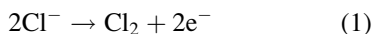
Ion-Exchange Membranes

in Chlor-Alkali Process,
Fig. 2 Illustrative scheme of the structure of different commercial membranes (de Bastos Vidal 2013; Vogel and Meier-Haack 2014)

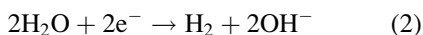


chloride ions are oxidized to chlorine gas. The sodium ions migrate through the membrane to the cathode compartment. The demineralized water added to the catholyte circuit is hydrolyzed, releasing hydrogen gas and hydroxide ions. The sodium and hydroxide ions combine to produce caustic soda which is typically brought to a concentration of 32–35 % by recirculating the solution before it is discharged from the cell. The reactions evolved in this process are the following (IPPC 2014):

At the anode:



At the cathode:



Depleted brine is discharged from the anode compartment and re-saturated with salt. If needed, to reach a concentration of 50 % caustic soda, the caustic liquor produced has to be concentrated by evaporation (using steam).

The first generation of commercial membranes (1975) was able to directly produce sodium hydroxide solutions of 2–40 wt %. They were made from fluoropolymers functionalized with sulfonic groups. These membranes were relatively thick with heavy reinforcement cloths and the electrode gap was 9 mm. Due to these membrane characteristics, the typical operating potentials were high (3.8–4.0 V at 2.5 kA/m²) that combined with low current efficiency give a DC energy consumption of 3300 kWh/ton of caustic soda. Additionally, the current efficiency decline

was quite fast due to impurities in precipitation in the membrane structure. Later on, the development of a laminated membrane structure with two different functional groups revolutionized the chlor-alkali membrane cell process by improving the current efficiency and reducing the operating potential (Navin 2002; de Bastos Vidal 2013).

Nowadays, the commercially available membranes in the chlor-alkali industry may have from one up to three layers but generally consist of two layers with a polymeric matrix made of tetrafluoroethylene. Sulfonic and carboxylic groups are used as fixed ionic groups on the anode and cathode side of the membrane, respectively (Fig. 2).

The use of different ionic groups, as illustrated in Fig. 2, has significant effects on the permselectivity and conductivity of each layer. Furthermore, the sulfonic groups are excellent proton conductors while the carboxylic groups are highly permselective to cations due to their lower water content (Sata 2000). The membranes must remain stable while being exposed to chlorine on one side and a strong caustic solution on the other. The mechanical properties of the membranes (tensile and tear strength) are greatly improved by reinforcements; a PTFE woven cloth is used to reinforce the membrane structure to prevent damage or tearing of the membrane. There are different types of cloths to reinforce the membranes and in some cases sacrificial fibers are also used. More and thinner fibers increase mechanical strength besides providing low voltage and high current efficiency. To prevent the adherence of bubbles to the membrane surface, the membrane surfaces are made hydrophilic. The

general economic lifetime of chlor-alkali membranes is approximately 3 years but ranges between 2 and 5 years (Strathmannm 2004; de Bastos Vidal 2013).

The perfluorinated membranes developed for use in chlor-alkali cells exhibit super selectivity and high thermal and chemical stability, which are not found in other classes of polymeric ion-selective membranes. There are four main manufacturers of ion-exchange membranes to the chlor-alkali industry: DuPont (Nafion membranes), Asahi Glass (Flemion membranes), Solvay Plastics (formerly Dow membranes), and Asahi Kasei (Aciflex membranes). The differences between suppliers are related to the modifications made on the polymer and on the functional groups, the type of reinforcement used, and other chemical and mechanical details (O'Brien et al. 2005).

The membranes commercially available for the chlor-alkali industry can be divided in two classes regarding their characteristics: high performance and high mechanical strength membranes. Low-resistance membranes are more adequate to narrow gap electrolyzers due to their low voltage. On the other hand, high-strength membranes are used in more robust electrolyzers where the main requirement is high physical strength. Today, membranes operate at higher current densities with current efficiencies of about 97 % producing a caustic soda stream of 32 wt %. The typical DC energy consumption values are as low as 2100 kWh/ton of caustic soda.

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Ion-Exchange Mosaic Membranes

► Mosaic Membranes

Iron Oxides: Polymer Composite Membranes

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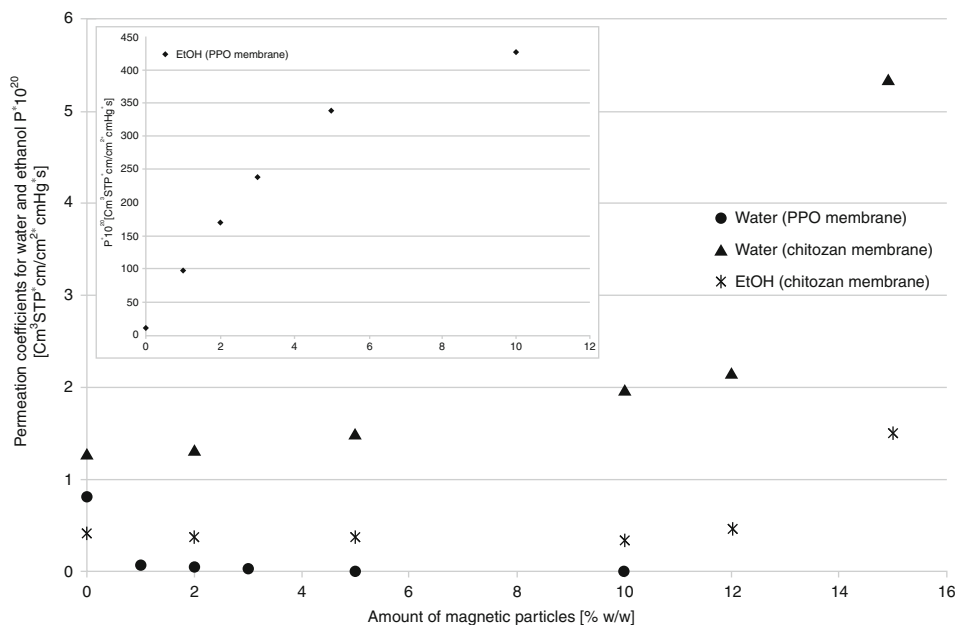
One of the best modification techniques for enhancing membrane performance is blending with inorganic nanoparticles such as iron oxides (Dudek et al. 2012, 2013, 2014), ZrO₂ (Gestel et al. 2006), TiO₂ (Gestel et al. 2006; Hong et al. 2013), Al₂O₃ (Hong et al. 2013), and carbon nanotubes (Gethard et al. 2011). In hybrid membranes, inorganic components are dispersed in a polymer matrix. These membranes benefit in the selectivity of active components and the simplicity of polymeric membrane processing. Particularly, the usage of inorganic-organic composite materials is becoming increasingly important due to their extraordinary properties, which arise from the synergism between the properties of the individual components as well as their interactions with the base matrix materials

(Dudek et al. 2012). The separation properties of the final composite membranes depend on component compatibility and dispersibility of the inorganic phase in the polymer matrix. Polymer grafting on the surface of the inorganic nanoparticles seems to be the best modification method for the dispersibility improving of the inorganic phase in the polymer matrix. Another surface modifiers often used for the stabilization of particles are fatty acids (oleic, lauric, palmitic, or stearic). Using those modifiers, the inorganic components could be well dispersed in polymer solutions forming uniform dispersion (Liu and Su 2005). In the case of higher concentration of inorganic phase in polymer solution, sedimentation phenomenon can be observed and further aggregation and inhomogeneous distribution, what was discussed in Dudek et al. (2012).

In recent years, the nanocomposite membranes, as a special functional material, have attracted much attention and been applied in loading of biomolecules (Nicolás et al. 2013), biosensor (Chena et al. 2012), metal adsorption (Stopa and Yamaura 2010), and others (Tsai et al. 2010). Especially, Fe_3O_4 ferrite magnetic nanoparticles (Dudek et al. 2012, 2013, 2014) have been rising as a significant useful material due to their specific properties such as superparamagnetic, nontoxic, great surface/area ratio, small size, etc. These materials exhibit novel macroscopic magnetic properties due to the combined action of quantum-sized effects, strain and surface effects, interface between nanostructures and the matrix, matrix properties, and morphologies of nanostructures. Compared to the traditional micro-sized magnetic supports used in separation process, nano-sized magnetic carriers possess quite a good performance due to higher specific surface area and lower internal diffusion resistance (Dudek et al. 2012, 2013, 2014). Iron oxide nanoparticles are being extensively exploited in several scientific and technological applications such as separation processes (Dudek et al. 2012, 2013, 2014), targeted drug delivery (Saboktakin et al. 2010), magnetic resonance imaging (Andreas et al. 2012), hyperthermia and cancer therapy (Santhosh and Ulrih 2013), water remediation (Crane et al. 2011), etc. Depending

upon the synthesis method and conditions, iron oxide can be obtained in one of several phases, such as FeO (wustite, antiferromagnetic), Fe_3O_4 (magnetite), $\text{Fe(II)Fe(III)}_2\text{O}_4$ (ferromagnetic or superparamagnetic when the size is less than 15 nm), $\alpha\text{-Fe}_2\text{O}_3$ (hematite, weakly ferromagnetic or antiferromagnetic), $\gamma\text{-Fe}_2\text{O}_3$ (maghemite, ferromagnetic), $\epsilon\text{-Fe}_2\text{O}_3$, and $\beta\text{-Fe}_2\text{O}_3$ (Si et al. 2008), among which magnetite and maghemite are the very promising and widely tested candidates for separation application.

The presence of magnetic particles in polymer matrix changes the transport mechanism. Changes in hydrophobicity/hydrophilicity balance of nanocomposite membrane containing metal oxide were reported by Balta et al. They noticed that even ultralow concentration of embedded ZnO nanoparticles (0.035 w/w %) into PES matrix had an important impact on the increasing of membrane hydrophilicity (Balta et al. 2012). Dudek et al. (2012, 2013, 2014) investigated the influence of iron oxide nanoparticles on chitosan and PPO (poly(2,6-dimethyl-1,4-phenylene oxide)) membrane separation properties. In both cases, the addition of magnetite nanoparticles to the polymer matrix has an impact on separation of ethanol/water mixtures. The main important changes in transport properties are observed comparing membranes without and with the iron oxide nanoparticles. The diffusion coefficient increases for one component and decreases for the other with a larger amount of magnetite powder. For the hydrophobic PPO membrane, the component preferentially passing through the membrane is ethanol. It has little tendency to absorb water, so that a droplet remains on the surface. The opposite situation occurs for the hydrophilic membranes. Hydrophilic membranes have an affinity for water. Their surface chemistry allows these materials to be wetted immediately. For such membranes, water preferably passes through the membrane. Comparing the separation properties of both discussed membranes on the basis of permeability coefficients, it can be observed that the poly(2,6-dimethyl-1,4-phenylene oxide) with magnetite addition has better separation properties than the hybrid chitosan membrane. It is demonstrated by the



Iron Oxides: Polymer Composite Membranes, Fig. 1 The comparison of permeability coefficients of water and ethanol for PPO and chitosan membranes

greater difference between the received permeability coefficient for water and ethanol (Fig. 1). The fluxes and diffusion coefficient values also confirm this relation. Large difference between flux and permeation coefficient, for the same amount of magnetite, gives a chance for effective and efficient separation of ethanol/water mixture and gives a chance to concentrate ethanol solution by faster permeation of water from the feed. The reason of bigger difference between the water and ethanol permeability coefficient for hybrid PPO membrane is probably the fact that the iron oxide powder, which is added to the polymer matrix, has hydrophobic properties. The PPO matrix has also hydrophobic properties, so in this case the interaction between polymer matrix and ferroferric oxide particles is very good. The opposite situation is for chitosan membranes with hydrophilic properties. For such membranes, the polymer matrix and iron oxide powder give an opposite effect. As a consequence permeability coefficients for the component preferentially transported through the membrane are not able to reach as high values of transport coefficients as in the case of PPO membrane.

Theoretical Background

The basic law of a phenomenological, parabolic diffusion through a slab membrane of unit cross section is the Fick's law:

$$J = -D(\cdot) \frac{\partial c}{\partial x} \quad (1)$$

where J is the diffusion flux, c stands for the concentration of the diffusing species, and D is diffusion coefficient ($D(\cdot)$ dot stands for the group of variables x, t, c).

When the external force field acts, we rewrite Eq. 1 in the form:

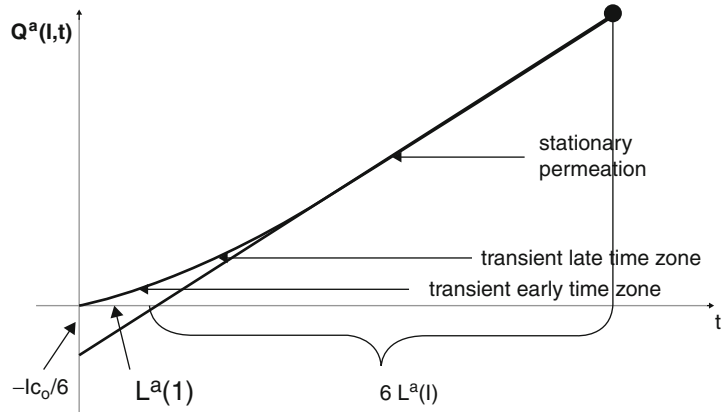
$$J = -D(\cdot) \frac{\partial c}{\partial x} + wc \quad (2)$$

where " w " is a drift coefficient (Strzelewicz and Grzywna 2007).

Crank and Park in (1968) reviewed the more useful experimental techniques for measuring diffusion coefficient. The most fundamental quantity, from many possible, is an average diffusion coefficient $\bar{D}$ calculated from the stationary permeation according to the evident formula, i.e.:

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Fig. 2 Schematic view of downstream absorption permeation curve



$$\bar{D}(\text{cm}^2/\text{s}) = \frac{J_s \cdot l}{\Delta c_0} \quad (3)$$

where J_s is a diffusive mass flux in a stationary state, l is the thickness of membrane, and Δc_0 can be obtained from an intercept of the asymptote to the stationary permeation curve with the $Q^a(l, t)$ axis (total flow of penetrant) (see Fig. 2).

Comparing $\bar{D}$ with the value of diffusion coefficient D_L calculated from the downstream absorption time lag (Grzywna and Łuczka 1991; Gadomski et al. 1993; Grzywna 1996; Grzywna and Stolarczyk 2005; Strzelewicz and Grzywna 2007, 2008; Rybak et al. 2009, 2012) (Fig. 2) according to the following equation:

$$D_L(\text{cm}^2/\text{s}) = \frac{l^2}{6L^a(l)} \quad (4)$$

we can get some insight into the nature of the transport process in question, namely, if $\bar{D} = D_L$, the diffusion is supposed to be an “ideal Fickian” unless there are some hidden processes, like a drift, which are beyond the reach of this simple protocol (Grzywna and Łuczka 1991; Gadomski et al. 1993; Grzywna 1996; Grzywna and Stolarczyk 2005; Strzelewicz and Grzywna 2007, 2008; Rybak et al. 2009, 2012). In fact, in the case of the “magnetic membranes,” the presence of a drift is almost certain. To calculate the realistic value of drift and the average diffusion coefficient, we should use a proper theory from which the following formula for time lag $\hat{L}^a(l)$ can be derived (Grzywna and Łuczka 1991;

Gadomski et al. 1993; Grzywna 1996; Grzywna and Stolarczyk 2005; Strzelewicz and Grzywna 2007, 2008; Rybak et al. 2009, 2012).

$$\hat{L}^a(l) = \frac{\bar{D}^2 \left(2 - 2e^{-(w/\bar{D})l} - 2\bar{D}wl + w^2l^2 \right)}{2w^3l} \quad (5)$$

Based on the first Fick's law, we obtain the equation for permeation coefficient determination (Dudek et al. 2013):

$$P = \frac{J_s \cdot l}{\Delta p} \quad (6)$$

where:

P – permeation coefficient [Barrer]

l – membrane thickness [cm]

Δp – difference of gas pressure at both sides of the membrane [cmHg]

J_s – diffusive mass flux [$\text{cm}^3_{\text{STP}}/\text{cm}^2 \cdot \text{s}$]

Diffusive mass flux is defined as:

$$J_s = \frac{Q_{\text{STP}}}{A} \quad (7)$$

where:

Q_{STP} – flow rate at standard condition [$\text{cm}^3_{\text{STP}}/\text{s}$]

A – membrane active area [cm^2]

Flow rate at standard condition is defined as (Dudek et al. 2013):

$$Q_{STP} = Q \cdot \frac{T_{STP} \cdot p}{T \cdot p_{STP}} \quad (8)$$

where:

Q – measured flow rate [cm^3/s]

p – atmospheric pressure [Pa]

T – atmospheric temperature [K]

p_{STP} – standard pressure, $p_{STP} = 1.013 \cdot 10^5$ Pa

T_{STP} – standard temperature, $T_{STP} = 298,15$ K

The solubility coefficient is a measure of the size of the sorption in membranes. It is characterized by division of the penetrant between the membrane and the outer phase in equilibrium. This parameter is calculated from the relation:

$$S = \frac{P}{D} \quad (9)$$

where:

S – solubility coefficient (distribution) $\left[\frac{\text{cm}^3_{STP}}{\text{cm}^3 \cdot \text{cmHg}} \right]$

Ideal selectivity coefficient could be given by quotient of given permeation coefficients:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (10)$$

where P_i , P_j is the permeation coefficient of separated components.

Membrane Preparation

Polymer membranes containing iron oxide nanoparticles were prepared using suitable polymer as a matrix, but first of all ferroferric oxide particles were prepared using the precipitation method described elsewhere (Khalafalla and Reimers 1980). For example, 12 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 24 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were each dissolved in 50 ml of water and combined into a 600 ml beaker with addition of 50 ml of concentrated ammonium

hydroxide solution (24 %). The decanted precipitate was washed twice by mixing with a diluted ammonium hydroxide solution (5 ml of ammonium hydroxide in 95 ml of water). After the second washing, the volume of precipitate slurry was adjusted to 50 ml and 4 g of dodecanoic acid (lauric) was added. The next mixture was continuously stirred and heated for 2 min using 550 W laboratory heating plate. Obtained stable magnetite fluid, after filtration in a solid state, was used for preparation of membrane.

Hybrid polymer membranes were prepared by cast method. For this purpose polymer (powder) was dispersed and dissolved in appropriate solvent (Dudek et al. 2012, 2013). After dissolution, the magnetite nanoparticles were added to the polymer solution. For proper dispersion and homogenization of iron oxide particles in the polymer solution, the mixture was sonificated using high-intensity ultrasound radiation. Sonification time was 30 min. After mixing, the solutions were poured into the Petri dishes, placed on the leveled plate, and then evaporated at room temperature for 24 h. In the case of hydrophilicity membranes, the suitable cross-linking agent was applied.

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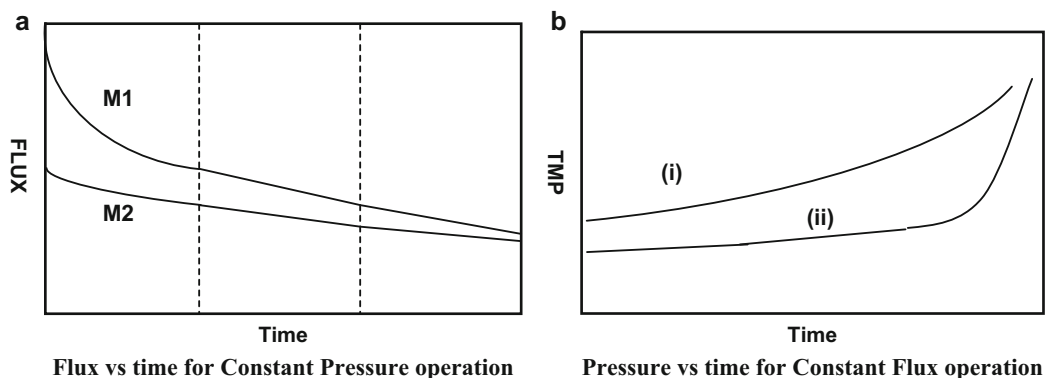
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Irreversible Flux Decline

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Membranes are either operated at constant pressure (P) or constant flux (J); the former is more typical of lab scale studies and the latter of commercial operation. Fouling leads to flux decline under constant pressure or a rise in the required transmembrane pressure ΔP for constant flux. These trends are illustrated in Fig. 1. It should be noted that fouling under constant pressure becomes self-limiting; the lower the flux, the slower the fouling. For constant flux operation, the fouling can be self-accelerating, often leading to a sudden rise in TMP (ΔP) as shown for case (ii) in Fig. 1b. This “TMP jump” could be associated with a critical consolidation of the fouling layer and rapid rise in fouling resistance.



Irreversible Flux Decline, Fig. 1 Constant pressure and constant flux operation: fouling trends

Irreversible flux decline is the drop in flux due to irreversible fouling. The effect of irreversible fouling can also be expressed as irreversible permeability decline (given by the change in $J/\Delta P$), and this can be used for both constant pressure and constant flux operation. However, it is important to note that fouling is flux driven. As a result it is more appropriate to compare membranes at the same initial flux for constant pressure tests. Figure 1a illustrates two membranes, M1 and M2, where M1 has an initially higher permeability and starts at a higher flux. Fluxes for M1 and M2 both decline due to the increasing fouling resistance (see ► [Irreversible Fouling Resistance](#)), and both membranes asymptote to similar declined fluxes. This is due to the eventual dominance of the fouling resistance (R_F) over the membrane resistance (R_m) (see Eqs. 1 and 2 in ► [Irreversible Fouling Resistance](#)). If membranes M1 and M2 were tested at the same constant flux, it would be easier to identify if one was intrinsically less prone to fouling.

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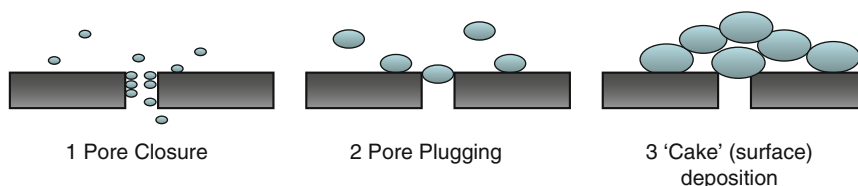
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Irreversible Fouling

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Membrane fouling is the accumulation of material on the surface of or within the membrane structure. The foulant may provide a cake or surface deposit layer, and if the membrane is microporous, the foulant could cause pore restriction/closure or pore plugging. These fouling mechanisms are depicted in Fig. 1. Membrane fouling is prevalent in all the liquid-phase membrane processes. Fouling species can be organic macromolecules (proteins, polysaccharides, etc.), inorganics (scale precipitates), and colloidal or biological (biofilms). Fouling is linked to, but different from, concentration polarization (CP). CP is a buildup of retained species (solutes) adjacent to the membrane surface and can be depicted as a boundary layer concentration profile based on a balance between convection (flux driven) and back transport (diffusion). CP increases with flux but is totally reversible when flux is ceased;



Irreversible Fouling, Fig. 1 Membrane fouling mechanisms

fouling is not totally reversible. In many situations fouling has both reversible and irreversible components. The reversible component may be removed by hydrodynamic means, such as back-wash or increased shear at the membrane surface. This type of foulant is usually loosely deposited or bound on the membrane and subject to removal by raised liquid velocities. However, it is not removed by simply dropping flux to zero. The irreversible fouling is material that is tightly held by the membrane. It could be colloids plugging pores, macrosolutes bound by adsorption, insoluble salts spreading as crystals, and biofilms comprising bacteria held in a matrix of extracellular polymeric substances (EPS). Irreversible fouling can usually be mitigated by feed pretreatment, suitable hydrodynamics, and careful membrane selection. For example, pretreatment could remove colloids or bacteria, or involve the addition of antiscalants. Hydrodynamic control could match crossflow velocity to the imposed flux to operate below the critical flux, where the critical flux is the flux below which fouling is negligible. Membrane selection would consider pore size, surface charge, hydrophobicity/hydrophilicity, etc. Irreversible fouling is usually partially removable by cleaning regimes, which could range from daily to monthly, with chemical or physical agents, depending on the situation. However, the gradual buildup of residual irreversible fouling, over multiple cleaning cycles, may eventually reach a critical level, and membrane replacement is required.

For more information on membrane fouling, see “► [Irreversible Flux Decline](#)” and “► [Irreversible Fouling Resistance](#).”

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Irreversible Fouling Resistance

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Flux can be related to the driving force ($\Delta P - \Delta \Pi$) and the overall resistance, R_T , by,

$$J = \frac{\Delta P - \Delta \Pi}{\mu(R_T)} \quad (1)$$

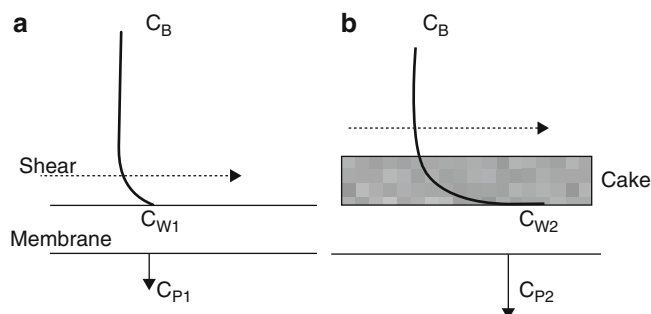
The osmotic pressure term ($\Delta \Pi$) can be ignored for non-osmotic operation (i.e., MF applications). The resistance components are assumed to be in series, so,

$$R_T = R_m + R_F \quad (2)$$

where R_m is the membrane resistance and R_F is the fouling resistance, which may comprise a reversible ($R_{r,f}$) and irreversible ($R_{ir,f}$) component, i.e.,

Irreversible Fouling Resistance, Fig. 1 (a)

Concentration polarization – clean membrane. (b) Cake-enhanced concentration polarization – fouled membrane



$$R_F = R_{rr} + R_{ir} \quad (3)$$

For a given ΔP , the flux vs. time data gives the various resistances. The initial clean water flux gives R_m , the final “fouled” flux gives R_T , and $R_T - R_m$ gives R_F . A water flush should remove R_{rr} , leaving resistances $R_m + R_{ir}$. Chemical cleaning should remove R_{ir} , but usually a residual ΔR_{ir} remains as explained in irreversible fouling. For constant flux, the ΔP data can be used to estimate the various resistances.

For processes like reverse osmosis, the osmotic pressure term in Eq. 1 is important. The magnitude of $\Delta \Pi$ is increased in practice by a factor M , the polarization modulus; this is due to concentration polarization. Equation 1 becomes:

$$J = \frac{\Delta P - M \Delta \Pi}{\mu(R_T)} \quad (4)$$

M is the ratio of solute concentration at the membrane surface to the solute in the bulk, and in a well-operated RO desalination process, without fouling, $M = 1.1$ – 1.2 . The polarization modulus, M , can be increased if there is a “cake” layer on the RO membrane surface. The layer provides an unstirred region where the solute (salt) concentration builds up. Figure 1 depicts concentration polarization for a clean and cake fouled RO membrane. The increased polarization (Fig. 1b) is “cake-enhanced” concentration polarization (CECP), and the increased osmotic pressure is the “cake-enhanced” osmotic pressure (CEOP) (Hoek and Elimelech 2003). Both fouling resistance and CEOP contribute to loss of flux (for fixed ΔP) or increased ΔP for fixed flux.

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Further Reading

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Isotherm Palladium Phase Diagram

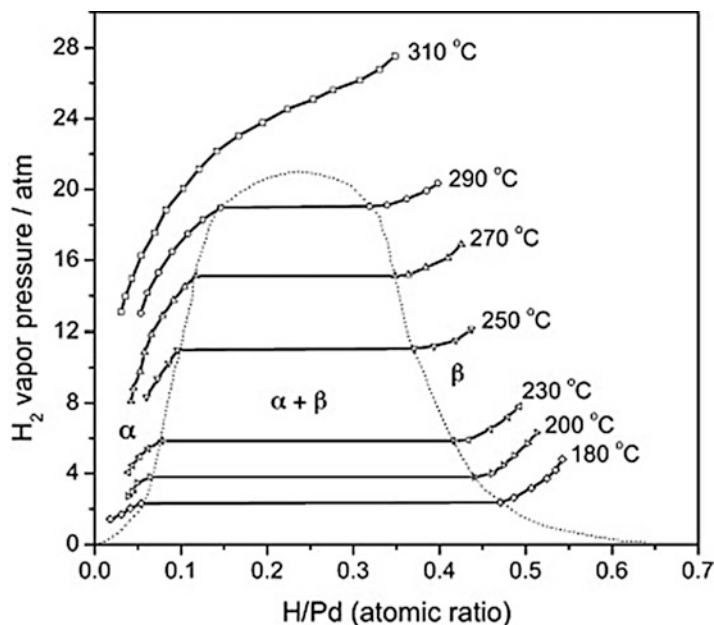
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Isotherm palladium phase diagram represents the palladium–hydrogen system as a function of pressure, temperature, and H/Pd concentration as shown in Fig. 1.

The isotherm palladium diagram is used to show the nature of one of the biggest problems of pure palladium membranes: hydrogen embrittlement. As shown in Fig. 1, the absorption of hydrogen below its critical point of 571 K (298 °C) and 2 MPa produces two different phases (α and β), both of which retain the pure palladium face-centered cubic (fcc) lattice but with the crystal unit cell lattice parameter increasing from 0.3890 nm for hydrogen-free palladium to 0.3895 nm for the α -phase and up to 0.410 nm

Isotherm Palladium Phase Diagram,

Fig. 1 Pressure–concentration–temperature phase diagram of the palladium–hydrogen system (Lewis 1967)



for the β -phase at room temperature (Lewis 1967; Ohira et al. 1996). The α -phase is obtained at low H/Pd atomic ratios and becomes the dominant phase at high temperature. The β -phase is formed at high H/Pd atomic ratios and coexists with the α -phase at low temperature (Fig. 1). The hydrogen vapor pressure is constant in the region of phase coexistence and is bounded by an envelope defining $\alpha_{\max}$ and $\beta_{\min}$, the compositions of maximum and minimum H/Pd ratio for pure palladium (Yun and Oyama 2011). The change in volume accompanying the phase transformation can give rise to strain and, consequently, after a few cycles to a metal lattice distortion (Shu et al. 1991), and micro-failures inside the metallic bulk are induced.

The alloying of palladium with other metals, lowering the coexistence temperature of the two crystalline phases, reduces the internal strength generated and avoids micro-failure formation inside the alloy bulk. Silver is the most used metal for avoiding hydrogen embrittlement phenomenon in Pd–alloy membranes. The critical temperature for the formation of β -phase of Pd–Ag alloy with a composition of 77 and 23 (%wt) is around room temperature (Paglieri and Way 2002).

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Isotope Separation, Membrane for

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The use of membranes for the separation of isotopes is one of the first practical applications for membrane processes. The first application was based on the effects that were described in 1846

by Thomas Graham, as a phenomenon of molecular effusion, i.e., differentiated flow rate of gases through small holes. When a mixture of two gases in a closed vessel is allowed to permeate through the porous barrier, assuming an equal concentration of the two gases, the molecules of the lighter component strike the barrier more frequently than the molecules of the heavier gas. If the holes of the barrier are sufficiently small to avoid convection flow (flow by volume) of gas and large enough to allow passage of the individual molecules, then the lighter molecules escape more readily through the pores and the permeate is enriched in the light component. The efficiency of partitioning is described by separation factor α expressed as the ratio of mole fractions of separated components after and before passing through the porous barrier or as the square root of the inverse ratio of the corresponding molecular weights:

$$\alpha = \frac{y(1-x)}{x(1-y)} = \sqrt{\frac{M_2}{M_1}}$$

where x and y are mole fractions of two separated isotopes and M_1 and M_2 are molecular weights of these components of the isotopic mixture.

In 1895 Rayleigh and Ramsey have separated argon and nitrogen using this method, and in 1920 Aston employed molecular effusion for enrichment of neon-22 isotope. Large improvement of the technology was achieved by Gustav Ludwig Hertz who developed the separating cascade, which was composed of several diffusion stages. They also used of the 24-stage cascade in 1932, which almost completely separated isotopes of neon, and by applying of the 48-stage cascade, they have separated isotopes of hydrogen. In 1936 Wooldridge, Jenkins, and Smythe have enriched isotopes of neon, hydrogen, and carbon in methane with 34-stage cascade. The most spectacular application of molecular effusion was enrichment of uranium-235 in natural uranium for military purposes within the frames of Manhattan Project during the Second World War. The all of the mentioned processes of separation of isotopes were carried out in the gas phase. In case of uranium isotope separation, the gas applied in

the process was uranium hexafluoride, UF₆. The membrane material had to be chemically resistant in this case, since the uranium hexafluoride used to produce enriched uranium-235 is highly corrosive (easily converted into hydrofluoric acid and harmful oxyfluorides as UO₂F₂). The important parameters of the molecular effusion barrier are the pore diameter and the permeation rate since according to the theory of molecular effusion, the diffusion transport through the membrane is selective when the pore size is commensurate with the mean free path of the molecules under the given conditions.

Also the large plants employing the molecular effusion (which is also called molecular diffusion or gaseous diffusion) were built in the United States with the most famous K-25 plant in Oak Ridge, Tennessee. The other systems were constructed in 1950s at Oak Ridge, Paducah, Kentucky, and Portsmouth, Ohio, in the United States, Capenhurst in England, and at Pierrelatte and Tricastin in France. There are also some reports on gaseous diffusion plants in the former USSR, Great Britain, Argentina, and in the People's Republic of China (Kirk-Othmer 1997). Today, the gaseous diffusion is an important method for uranium-235 enrichment, despite the competitiveness of the centrifugal methods. This is used in the United States and France, including Eurodif, led by France, Italy, Spain, and Belgium, which holds the plants in Tricastin and Pierrelatte (France).

For preparation of membranes, different methods are applied: etching with strong acids (alloys of gold and silver), sintering and extrusion of fine metal powders and oxides of metals (nickel, aluminum oxides), and the anodic oxidation (aluminum oxides). Typical gas diffusion membrane has a pore size of 0.006–0.04 mm and operates at temperature of 60–200 °C and at pressure of 0.4–3.3 bar. Support layer of the membrane is a porous material with a pore size of 2–10 mm. Ceramic and metallic microporous membranes were applied for separation of isotopes, including other than uranium, such as isotopes of argon, neon, and hydrogen. Although information about the materials used for manufacturing gaseous diffusion membranes are very scarce, it is known that French technology

used sintered anode and aluminum, alloys of gold and silver, nickel, Teflon, porcelain (Burggraaf and Cot 1996), and zirconium (Hsieh 1996).

Attempts of using the polymeric membranes for the separation of isotopes of hydrogen with membranes made of polymers, such as polyethylene terephthalate (PET), polyethylene (PE), polytetrafluoroethylene (PTFE), cellulose acetate (CA), and plasticized polyvinyl chloride (PVC), were taken by Marcea (1983). Although the selectivity of polymers is lower than metallic membranes, it is worthy to point out, since the numerous benefits of their use, such as the low-cost of membranes, the possibility of formation of capillaries resulting in large areas for permeation, and no need of high pressures and temperatures.

The studies on separation of hydrogen and oxygen in the liquid phase (water) were carried out in Pacific Northwest Laboratory, USA (Nelson et al. 1996). Polymeric membranes were used in Institute of Nuclear Chemistry and Technology, (Poland). They were made of regenerated cellulose, cellulose acetate (Chmielewski et al. 1991), and polytetrafluoroethylene (Zakrzewska-Trznadel et al. 1996). The economic assessment showed that membrane permeation is competitive with other methods of hydrogen and oxygen isotopes separation. The demand for heavy oxygen water, due to the development of PET diagnostic method, has intensified the interest in new processes of separating isotopes of oxygen, among others – membrane method (Kim et al. 2004).

The following isotopes of chlorine (Campbell 1985), carbon (Fritz et al. 1987), lithium (Whitworth et al. 1994) in aqueous solutions, and uranium (Okamoto et al. 1980) in ammonia were separated by means of various membrane techniques and by using of different membranes. Gadolinium and neodymium isotopes were separated by means of a hybrid complexation/nanofiltration (Chitry et al. 2001) processes. The new complexing agents and ligands, which were

used in the hybrid process, were developed based on DTPA (see also Chitry et al. 2001).

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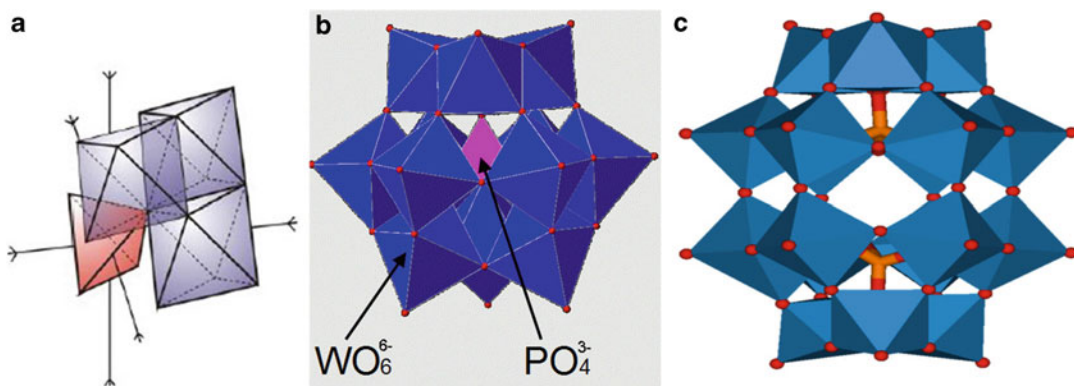
Keggin Structure

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Heteropoly compounds (HPCs) have an almost two centuries-long history. Since 1826, when the first polyoxometalate (POM), $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$, has been synthesized (Berzelius 1826), they are well known as analytical reagents, catalysts, and biochemical and biomedical active compounds (Rhule et al. 1998; Kuntić et al. 2006). The best known group of POMs are those where heteroatoms are surrounded by a cage of transition metals ($\text{M}=\text{Mo}$ and W), as a result of Mo and W acids polymerization. Two structure types predominate in this group of compounds: Keggin ions $[\text{X}^{n+}\text{M}_{12}\text{O}_{40}]^{(8-n)-}$ synthesized in 1934 (Keggin 1934) and Dawson or Wells-Dawson ions $(\text{X}^{n+})_2\text{M}_{18}\text{O}_{62}^{(16-2n)-}$, with structure determined in 1953 (Pope 1983) (Fig. 1). It is evident from Fig. 1a how Keggin anion is formed. On each corner of central tetrahedron, three WO_6 octahedra are bonded sharing corners and sides. Thus, such group could be presented as an M_3O_{13} group. It is possible to distinguish four oxygen atoms in such structure: O_1 (terminal), O_2 (edge bridging), O_3 (corner bridging), and O_4 atoms shared with central tetrahedron. Typically,

heteroatoms are phosphorus (P) and silicon (Si); nevertheless, some other metals such as V , Nb , Ta , and U also show comparable behavior, but to a more limited extent. Bands in IR and Raman spectra, characteristic for host lattice, and used for quick and ease identification of POMs, are assigned to PO_4^{3-} group (at about 1,003, 988, and 983) $-\nu_1$ stretching and at 516 cm^{-1} are assigned to PO_4^{3-} asymmetric bending vibrations. Some other bends are assigned to groups of addenda atoms: about 805 to $\text{W}-\text{O}-\text{W}$ asymmetric stretching, at 536 to $\text{W}-\text{O}-\text{W}$ symmetric stretching, and 273 cm^{-1} $\text{W}-\text{O}-\text{W}$ bending vibrations. Below 450 cm^{-1} lattice modes are expected (Rocchiccioli-Deltcheff et al. 1983; Mioč et al. 1994). Keggin anions form channels full with water and hydrated protons (cf. “Heteropoly Acids”).

POMs of Mo and W are of two types, isopolyoxometalate and heteropolyoxometalate, which contain one or two atoms of another element (heteroatom) besides molybdenum or tungsten, oxygen, and hydrogen. More than 65 elements from all groups of the periodic table can be found incorporated into polyoxoanions as heteroatom. Covalent attachment of amino acids as glycine, alanine, and lysine to POMs is also possible. Such compounds are interesting especially for the investigation of biochemical and biomedical activity of HPCs (Rhule et al. 1998; Kuntić et al. 2006).



Keggin Structure, Fig. 1 Three predominate structure of POMs: (a) group of three WO_6 octahedra around central PO_4 tetrahedron of Keggin anion; (b) primary structure of Keggin anion; (c) Dawson's structure

After the discovery of their superionic proton conductivity ($\sigma = (1\text{--}100) \times 10^{-3}$ S/cm) at room temperature in 1979 by Nakamura et al. (1979, 1981), the chemical and electrochemical conductive properties of these selected compounds have become very interesting as new materials, potentially useful for different solid-state devices: as sensors, proton exchange membranes (PEM) in H_2/O_2 fuel cells, electrochromic displays, and ion-selective membranes (Colomban 1992). Proton conductivity (not lower than 1×10^{-4} S/cm) is necessary to enable the use POMs as PEM in fuel cells, or in batteries (Mioč et al. 2005; Holclajtner-Antunović et al. 2010; Mentus et al. 2010). But regrettably they also have some deficiencies. They are sensitive to ambient conditions: relative humidity (RH) and temperature. Also, they have low specific surface area ($20\text{--}30$ m^2/g) and are washable from PEM. These deficiencies may be avoided if HPCs are incorporated in composites, and/or polymers, and also if POMs are used as acid insoluble salts of heteropoly acids, or some other compounds, as bronzes, where HPCs have been used as precursors (Mentus et al. 2010).

The applications of POMs are associated with their size, high ionic weight and redox characteristics, polarity, surface charge distribution, electron and proton transfer/storage ability, the formation of high Brønsted acid centers, and so on.

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Kinetic Study in Bulk Liquid Membranes

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Kinetic study of the transport of different chemical species through bulk liquid membranes has been widely studied, including metallic ions (Cu^{+2} , Co^{+2} , Cr^{+6} , Hg^{+2} , Na^+ , Pd^{+2} , U^{+6}), anionic species (CN^- , SCN^- , Cl^-), dyes (methylene blue, cibacron red FN-R), amino acids (valine, phenylalanine), and other compounds. Most of these studies have employed carrier-mediated transport

mechanisms by using different types of carriers and organic diluents in the membrane phase and different stripping agents in the product phase. Dimensionless reduced concentrations of the target species in the feed (R_f), membrane (R_m), and product phases (R_p) were used ($R_f = C_{ft}/C_0$; $R_m = C_{mt}/C_0$; $R_p = C_{pt}/C_0$; the sum $R_f + R_m + R_p$ obviously being unity).

In most of these studies, the variation with time of the reduced concentrations of target species decreased monoexponentially in the feed phase, followed an increasing sigmoided-type curve in the product phase and presented a maximum in the membrane phase (Fig. 1).

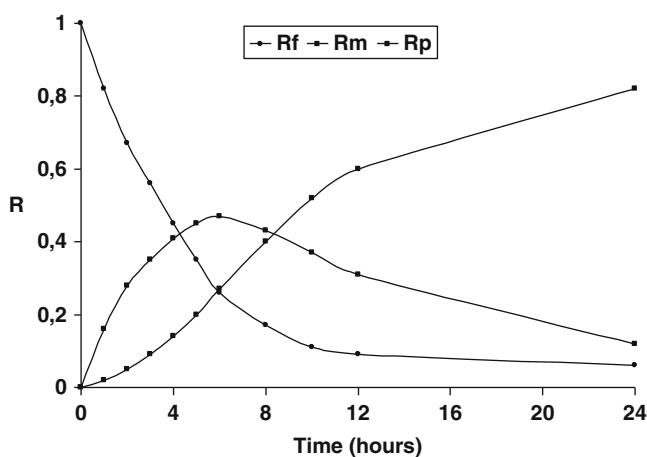
All these results suggest that target species transport through bulk liquid membranes by using a carrier mediated transport obeys the kinetic laws of two consecutive irreversible first-order reactions, i.e., the extraction (rate constant, k_{ex}) and the stripping (rate constant, k_{st}) reactions (Szpakowska and Nagy 1991; He et al. 2000; León and Guzmán 2005). The irreversibility is to be expected because R_f and R_m tend to be zero, while R_p tends to be one, that is, the transport from the feed phase to the product phase seems to be virtually complete. This kinetic behavior can be mathematically described according to the following equations:

$$\frac{dR_f}{dt} = -k_{ex}R_f \equiv J_{f/m} \quad \frac{dR_m}{dt} = k_{ex}R_f - k_{st}R_m$$

$$\frac{dR_p}{dt} = k_{st}R_m \equiv J_{m/p}$$

Kinetic Study in Bulk Liquid Membranes,

Fig. 1 Typical curves of time dependence of R_f in feed phase, R_m in membrane phase, and R_p in the product phase, in the transport of a chemical specie through a bulk liquid membrane by using a carrier facilitated transport



Integration of those differential equations gives $R_f = \exp(-k_{ex} t)$

$$R_m = \frac{k_{ex}}{k_{st} - k_{ex}} [\exp(-k_{ex} t) - \exp(-k_{st} t)]$$

$$R_p = 1 - \frac{1}{k_{st} - k_{ex}} [k_{st} \exp(-k_{ex} t) - k_{ex} \exp(-k_{st} t)]$$

These equations show that the time dependence of R_f is monoexponential and the time dependence of both R_m and R_p is biexponential.

R_m has a maximum $R_m^{\max} = \left(\frac{k_{ex}}{k_{st}}\right)^{-\frac{k_{st}}{k_{ex}-k_{st}}}$ at time $t_{\max} = \frac{\ln\left(\frac{k_{ex}}{k_{st}}\right)}{k_{ex}-k_{st}}$

Maximum fluxes can also be obtained:

$$\left[\frac{dR_f}{dt}\right]_{\max} = -k_{ex} \left(\frac{k_{ex}}{k_{st}}\right)^{-\frac{k_{st}}{k_{ex}-k_{st}}} = J_f^{\max}$$

$$\left[\frac{dR_m}{dt}\right]_{\max} = 0$$

$$\left[\frac{dR_p}{dt}\right]_{\max} = k_{st} \left(\frac{k_{ex}}{k_{st}}\right)^{-\frac{k_{st}}{k_{ex}-k_{st}}} = J_p^{\max}$$

$$-\left[\frac{dR_f}{dt}\right]_{\max} = +\left[\frac{dR_p}{dt}\right]_{\max} \Rightarrow -J_f^{\max} = +J_p^{\max}$$

Moreover, in many cases, the activation energy values of the processes were obtained from the Arrhenius equation, $\ln k = \ln A - \frac{E_a}{R \cdot T}$, by using the k_{ex} and k_{st} values at different temperatures.

Notwithstanding the previous comments, kinetic studies on Cu(II) transport through bulk liquid membrane containing 2-hydroxy-5-nonyl-benzaldehyde (Acorga P-50) as carrier in *n*-octane and sulphuric acid as stripping agent (Szpakowska and Nagy 2000) described that the $[Cu(II)]/[Carrier]$ ratio influences the kinetic regime. It was found in these studies that for $[Cu(II)]/[Carrier]$ ratio higher than 5, both the extraction and the stripping steps were of zeroth order with respect to copper, with remaining copper concentration in the membrane small and practically constant. When $[Cu(II)]/[Carrier]$

ratio was lower than 1, the process followed the kinetic laws of two consecutive irreversible first-order reactions, with reduced concentrations of Cu(II) decreasing monoexponentially in the feed phase, following an increasing sigmoided-type curve in the product phase and presenting a maximum in the membrane phase. Between these two ratio ranges, the kinetics was of intermediate character. These results show the possibility of changing the transport kinetics by varying the $[Target\ species]/[Carrier]$ ratio.

Cross-References

► [Carrier-Mediated Transport](#)

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Knudsen Diffusion

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Synonyms

[Knudsen transport modeling](#)

Whenever a species is diffusing inside a confined space, such as cylindrical pore, an interaction between the diffusive molecules and the pore

wall is to be expected. One possibility is given by the pore wall physically interacting with the diffusive molecules and hindering, as a consequence, their movement. The phenomenon, called Knudsen diffusion, is relevant whenever the distance between molecular collisions is greater than the pore diameter. This interaction can be the governing factor of the diffusion rates.

Liquid have a relatively small mean-free path, few angstroms, so that Knudsen diffusion is not important in practical cases, but on the other hand, for gas this parameter can assume values larger than 1,000 Å and therefore be significant.

The diffusion coefficient, D_{Kn} , in the Knudsen regime can be estimated from gas kinetic theory, and it is given by

$$D_{Kn} = 4850d\sqrt{\frac{T}{M}}$$

where d is the pore diameter in cm, T the absolute temperature, and M the molecular weight of the diffusive species. Unlike diffusion in unbounded systems, Knudsen diffusion coefficient is independent of pressure and of the molecular weight of the second species.

Cross-References

► [Principle of Gas Separation](#)

Knudsen Transport Modeling

► [Knudsen Diffusion](#)

Lamellar Copolymers

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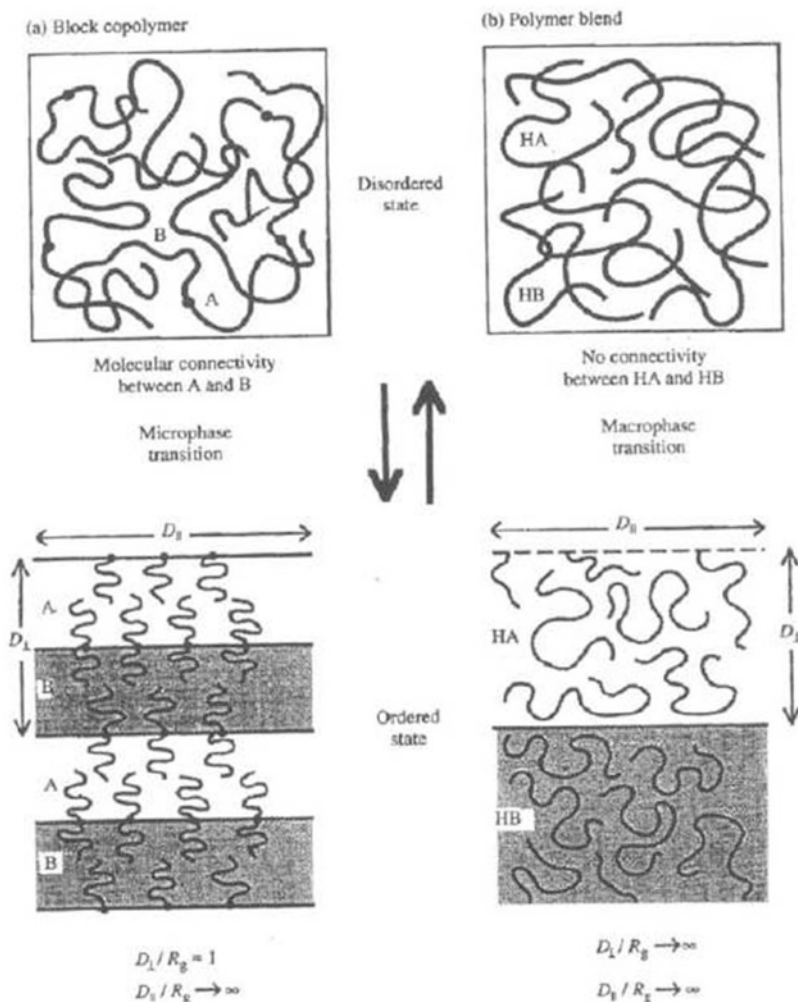
The presence of covalent bonds between the blocks in block copolymers leads to severe restrictions on the state of local segregation between them allowing the formation of few and defined morphologies. Comparing the phase separation that occurs in a pure copolymer AB and into the corresponding mixture of homopolymers HA/HB and assuming that in both cases strips of different phases are formed, parallel to the surface of the system, it is observed that in the mixture the size of the homopolymeric lamellae parallel to the surface and perpendicular to it are both much greater than the radius of gyration (R_g) of the polymer. Instead, in the case of the block copolymer, the presence of the bond between the blocks allows the formation of lamellae whose dimensions parallel to the surface are much greater than the radius of gyration, but the size perpendicular to the surface has dimensions comparable to the radius of gyration. On the basis of this different structural feature, the domains of different compositions which are formed in a mixture of homopolymers are named macrophases, while in the case of a copolymer are spoken of microphases or even, sometimes, of nanophases (Fig. 1).

There are numerous methods for inducing the orientation and order of large-scale morphologies of the copolymers blocks, such as lamellae. Some main strategies used are reported:

- Fields of mechanical flow (extrusion (Keller et al. 1970; Folkes et al. 1973), compression (Kofinas and Cohen 1995; Drzal et al. 2001; Quiram et al. 1998; van Asselen et al. 2004), flows involving oscillating (Skoulios 1977; Hadziioannou et al. 1979, p. 15, 1979, p. 136; Morrison and Winter 1989; Morrison et al. 1990; Wiesner 1997; Scott Pinheiro and Winey 1998; Leist et al. 1999; Hermel et al. 2002; Stangler and Abetz 2003; Wu et al. 2004) or stationary (Sebastian et al. 2002; Angelescu et al. 2004, 2005; Luo and Yang 2004) shear, or techniques that combine different flow fields (Albalak and Thomas 1993, 1994; Honeker et al. 2000; Dair et al. 2000; Villar et al. 2002)) were successfully used to induce alignment in block copolymers.
- Magnetic fields induce orientation in liquid crystalline block copolymers (Osuji et al. 2004; Tomikawa et al. 2005) and block copolymers with a crystallizable block through an accurate control of the crystallization process (Grigorova et al. 2005).
- Static electric fields have been widely used to guide macroscopically cylindrical and lamellar morphologies in the melt of such copolymers (Morkved et al. 1996; Onuki and Fukuda 1995;

Lamellar Copolymers,

Fig. 1 Phase separation in block copolymers (a) and in homopolymers blend (b) (Schulz and Bates 1996)



Thurn-Albrecht et al. 2000, 2002; Elhadj et al. 2003; Xu et al. 2004; DeRouchey et al. 2004; Xiang et al. 2004).

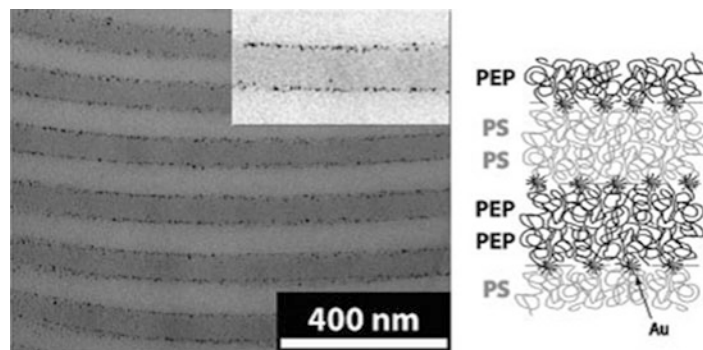
- Solvent evaporation allows the orientation of lamellar microdomains perpendicularly to the film surface (Turturro et al. 1995; Kim and Libera 1998, p. 2569, 1998, p. 2670). After the deposition, the glass transition temperature (T_g) of the film swollen with a solvent is below the ambient temperature, allowing free mobility of the chains. With increasing concentration of the solvent, the copolymer undergoes a transition from the disordered state to the ordered. The diffusion of the solvent in the thin film produces a concentration gradient so that

order spreads rapidly from the surface of the film to the substrate. The consequent decrease of T_g below room temperature, for at least one block, freezes the structures that, due to the high directionality of the solvent gradient, organize into domains with lamellar axes perpendicular to the surface (Kim et al. 2004; Kimura et al. 2003; Lin et al. 2002; Temple et al. 2003).

A great potential of the block copolymers is represented by the possibility of using the ordered nanostructures formed by self-assembly as a matrix (host) for the inclusion of guest molecules (guest) and dispersion of different types of

Lamellar Copolymers,

Fig. 2 Bright-field TEM image of a thin film of a lamellar block copolymer polystyrene-poly(ethylene-co-propylene) in which gold nanoparticles suitably passivated are included only in the layers of polystyrene (Bockstaller et al. 2005)



nanoparticles, in order to obtain nanocomposites with special physical properties. The nanocomposites represent a class of composite materials consisting of matrix and a polymeric particle reinforcement having at least one dimension of the order of nano; such particle reinforcements are called nanofillers or nanoreinforcement.

The different microdomain nanostructures generated by block copolymers (lamellae in particular, but also spheres or cylinders) act as host to sequester selectively nanofillers (guest) with a suitable chemical and geometrical affinity.

The great innovation of these studies consists in the fact that the use as a matrix of block copolymers, then nanostructured materials already, instead of homopolymers, offers an important opportunity to control the distribution of spatial and orientational nanofillers. The nanoparticles, which induce specific properties, are not, in fact, randomly distributed in the polymer matrix but are sequestered in ordered microdomains and, thus, distributed in an orderly manner in the matrix. This allows a greater control of the final physical properties of the nanocomposites. A TEM image of a thin film of a nanocomposite based on a lamellar block copolymer in which gold nanoparticles are distributed in such an ordered way only in specific layers of the structure is shown in Fig. 2 (Bockstaller et al. 2005).

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Langerhans Islet

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The **islets of Langerhans** are endocrine cell cluster well ordered in lobules, of 0.3–0.7 mm in diameter, containing from 3,000 to 4,000 cells, and located mainly in the tail region of the pancreatic gland. Discovered in 1869, though representing only 2 % of the whole organ, they serve to coordinate the physiological control of the glycemic values in the blood. Five different hormone-secreting cell types constitute the islets' cytoarchitecture: alpha cells producing glucagon, beta cells producing insulin and amylin, delta cells producing somatostatin, PP cells (gamma cells) producing the pancreatic polypeptide, and epsilon cells producing ghrelin. In human beings, the alpha and beta cells are in close relationship with each other. Representing nearly 90 % of the total islet cells, their secretive activity is modulated by the blood glucose levels: when low concentrations of sugar are detected, the islets respond with the glucagon secretion to induce the glucose release from the hepatic deposits into the bloodstream. After a meal the high concentration of the blood sugars causes the beta cell activation determining the insulin-induced glucose metabolism and the production of the energy requested by the body. Since the interaction between the hormone-secreting cells of the islets and the paracrine, electric, and nervous-regulating factors is highly complex, the tiniest decompensation in the islet cells' functions, modulation, and survival can result in the onset of severe pathologies and organic disorders, which leads patients to severe complications and a high risk of death. Actually, 98 % of the diseases involving the pancreas referred to the loss of the ability in modulating the food sugars' conversion into energy, due to the malfunctioning or destruction of the

insulin-producing beta cells by autoimmune responses. Thus, sustaining and/or replacing malfunctioning islets is the only therapeutic approach in order to induce the partial recovery of the metabolic functions in the patients (Patel et al. 2014). Before 1893 and the discovery of the pancreas involved in the income of the diabetes, starving was the only treatment possible for people suffering for diabetes. Then, first attempts in the development of grafts were made using deceased donor's islets serving as substitutes for the malfunctioning pancreas. Many patients showed a partial recovery; however, after transplantation, these islet grafts were inevitably destroyed due to the immune and inflammatory reaction in the hosts. In truth, despite the risk/benefit trade being quite high for the patients, *the transplantation* still remains the only therapeutically approved approach to gain the patients recovery of the pancreatic activity. Allo and autotransplantation are nowadays performed through the infusion of purified islets into the portal vein of the liver, and 50 % of the receivers are able to regain the pancreatic functionality and recover from the systemic complications in 1 year. However, the number of available and compatible donors is quite limited, and the lifetime immunosuppression therapy exposes the patient to infections, diseases, and harmful side effects. Thus, new techniques labeled as tissue engineering approaches have been developed to overcome these disadvantages and foresee the use of polymeric membrane systems to produce engineered device containing islets of insulin-producing cells, to control the release of the cell products from the islets, their sustainment, and their protection from the immunoreactive species in the site of implantation. Coordinated by local drug delivery systems, consisting in bores of low-dose anti-rejection drugs able to minimize the immune response as well as any inflammatory effects at the site of implantation, the *encapsulation* technique is the most promising method. The islets are wrapped in a tight coating made of biocompatible polymers acting as a perm-selectivity membrane that serves to mimic the heterogeneous and safe

environment where oxygen and nutrient perfusion is provided continuously and appropriate space and ECM-like physical and mechanical support, essential for the correct insulin production and secretion and the islets' survival, are provided. Different classes of encapsulating devices are available and classified depending on their size in macro-, micro-, and nano-devices. Classified as extravascular diffusion devices when placed subcutaneously or in the peritoneal cavity and intravascular diffusion system, three *macrodevices* have been approved for the clinical trials: *the TheraCyte system*, made up of two composite Teflon-based membranes in between the islets are placed; *the Islet Sheet device*, constituted by supported alginate sheets containing the pancreatic islets; and *the Beta O₂ device* able to increase the oxygen exchange in the implantation site being made of oxygen-generating biomaterial able to deliver locally the oxygen to the cells. Additional macrodevices consist of tubular porous membranes filled with islets generally placed into the vessels, where adequate kinetic properties allowed the insulin release straight into the blood stream. *Micro devices* constituted by single cluster of beta cells incorporate into semipermeable polymeric membranes, and *nano-devices* are nowadays under investigation in a few animal models. They differ generally on the processing methods used for the encapsulation of the islets and both allow to increase the insulin release rate and the oxygen exchange into the islets. The micro systems are processed in a spherical system of alginate hydrogels coated with poly-ornithine and polylysine or by cross-linking a thin hydrogel sheet onto an islet cluster by the *conformal coating* methods, whereas the nano-devices (1–100 µm) consist of islets encapsulated by alternating charged polylysine, polyglutamic acid, and PEG-biotin polymers over the cell aggregate surface through the *layer-by-layer method*. The decreased thickness of the capsules obtained by covering the islets with a single sheet of molecules increases and improves the insulin release kinetics after implantation and resulting as well in higher diffusion of nutrients in the core of the cell clusters. Independently on the size of the device, three different encapsulated

replacement strategies are available for the implantation: All-In/Biodegrade-Out replacement, made of biodegradable components easily absorbed by the body; All-In/All-Out replacement, designed to not react with the host tissues as the cytotherapeutics devices, the islet sheet medical devices, and the beta-O₂ device; and Flush/Reload replacement used for the macrodevices designed in order to grow into the host to provide a vascular interface (David and Marchetti 2014). *New cell sources*. To overcome the shortage of donor organs and the side effect linked to the autoimmune destruction of the patient islets as for diabetes type I, alternative sources of beta cells have been researched. The adult stem cells or progenitor cells appear to be the most promising. Through reprogramming cell strategy (transdifferentiation), pancreatic precursor cells are reprogrammed in insulin-producing cells. Moreover, the own patients pancreas exocrine cells and the skin cells that can undergo to the reprogramming technique representing a promising new source for the beta cells supply, being not needed the immunosuppression therapy after the implant (Dominguez-Bendala et al. 2013). Therefore, another potential source of beta cells may be the xenotransplantation with pig pancreas cells. Interestingly, human and porcine insulin differ only for one amino acid, and insulin extracted from porcine pancreas has been used for the treatment of patients with diabetes before the development of recombinant human insulin technology. However, several problems need to be overcome for porcine islet transplantation to become a viable clinical option; however, studies in rodents and large animals have shown great promise that justifies cautious optimism for the near future. In the last years, another chance to improve the tissue engineering of the pancreas appears to be the prevention of the inflammation at the site of the transplant, co-transplanting mesenchymal stem cells. The MSCs that have been demonstrated offer natural defenses by blocking the signals of the immune responses, limiting inflammation, stimulating the blood vessel growth, and promoting the long-term function of islets due to their trophic effects.

Up until now, though the most important progress in the pancreatic islet transplantation is

settled in preclinical trials and only one lead research project has been presented in the last years on baboons, 95 % of the patients who received the capsule implantation resulted in considerable improvements of the glucose metabolism with the reverse of the main diabetes side effects at 1 year and more than 80 % at 5 years after implants opening new hopes in the further improvement of new strategies for the diabetes treatment in the nearest future.

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Langmuir and Langmuir–Blodgett (LB) Films

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An ultrathin, resistant layer can be formed at the air-water interface by spreading a single drop of oil. This phenomenon was discovered centuries ago, but it was *Irving Langmuir* that in the early twentieth century established sound theoretical and experimental basis for their study (Langmuir 1917). The now-called Langmuir monolayers are formed at air-water interfaces using an experimental system known as Langmuir trough. Basically a solution containing amphiphilic molecules

(with both hydrophobic and hydrophilic parts) is spread over at the air-water interface. The hydrophilic parts allow the spreading of the molecules while the hydrophobic parts do not let the molecules dissolve into subphase. Movable barriers are used to compress the monolayer. The presence of the monolayer can be detected easily by measuring the surface pressure (π), which is the decrease in surface tension, as the monolayer is compressed, thus leading to pressure-area isotherms.

In the 1930s, *Katharine Blodgett* – then an assistant to *Langmuir* – developed the procedures to transfer the monolayer onto a solid substrate (Blodgett and Langmuir 1937). The deposited films are now termed Langmuir-Blodgett films. Basically, monolayers can be transferred by immersing (or withdrawing) the substrate into (or from) the liquid while the monolayer is adsorbed homogeneously at the substrate. Thus, well-ordered films with very accurate thickness can be formed.

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Layer-by-Layer (LbL) Method

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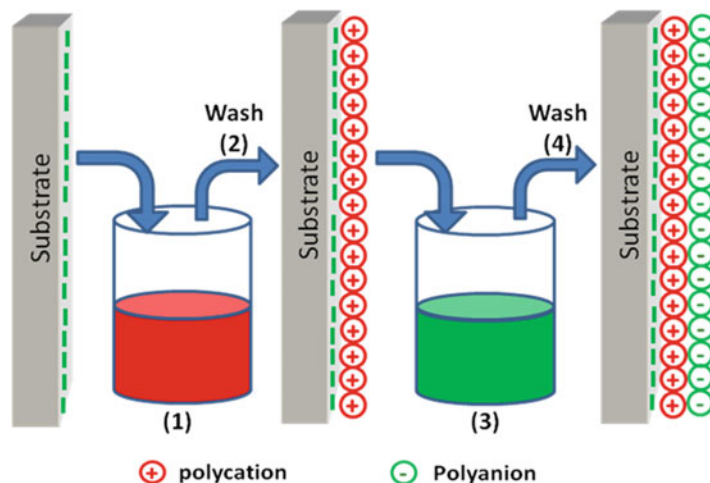
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Layer-by-layer (LbL) method (also known as LbL assembly, electrostatic self-assembly (ESA), or polyelectrolyte multilayer (PEM) technology) is

Layer-by-Layer (LbL) Method,

Fig. 1 Simplified schematic of the film deposition process using LbL method



a versatile method to form multilayers on a solid support. The self-assembly method is driven by the electrostatic force between the precursor materials. Precursor materials to form multilayers can be chosen from polyelectrolytes, biopolymers, clays, metal complex and their derivatives, nanoparticles, dendrimers, and so on (Bertrand et al. 2000). The advantages of this method are the relatively simple process, independence of substrate properties (i.e., size, topology, materials, and so on), and formation of fuzzy structure. Therefore, LbL method has a potential to be applied in various applications including forming multicomposite films, nanoparticle modification, enzyme process, optic development, sensors, membrane for water treatment, fuel cell, and so on.

The basic formation mechanism of a typical LbL process is shown in the schematic drawing in Fig. 1. Step (1) shows the absorption of polycation by a negatively charged substrate. After washing with deionized water (step (2)), the substrate was soaked in a polyanion solution (step (3)). Then, it is washed with deionized water (step (4)). These procedures can be repeated to prepare multilayers on the substrate. Other variations to this basic coating method includes spray (Schlenoff et al. 2000), spin (Chiarelli et al. 2001), hydrodynamic LbL deposition (Deng et al. 2008), electric field-induced LbL process (Zhang

et al. 2008), and pressure-induced LbL process (Zhang et al. 2011). Characteristics of the LbL films are known to be highly affected by the preparation procedures and conditions. In addition to the substrate and multilayer materials, other main factors affecting LbL film properties include ionic strength of coating solution, solution pH, coating time, and the use of cross-linkers.

Cross-References

► Cross-Linked Layer-by-Layer Membranes

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Layer-by-Layer Self-Assembly Membrane

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Layer-by-layer (LbL) self-assembly membranes are multilayered nanoarchitectures obtained by depositing oppositely charged polyelectrolytes or molecules presenting mutually interacting binding sites (Table 1) (Borges and Mano 2014). The LbL method can not only be applied to polymers but also on the combinations of polymers with particles.

The LBL assembly based on electrostatic interaction is the most used and investigated method for multilayered nanoarchitecture construction. In this case, LbL self-assembly membranes are produced by simply repeating the alternate immersion of a charged substrate in the corresponding polyionic solution of opposite charge (Fig. 1). To speed up the deposition process, otherwise time consuming as a consequence of the necessity to wait several minutes between each step of adsorption and rinsing, spray deposition and spin coating have been demonstrated to be suitable. The method is very attractive due to its simplicity and efficiency in film preparation; however, the multilayer assemblies are less stable and robust than the ones obtained by hydrogen or covalent bonding.

The LBL growth, structure, and properties of multilayer assemblies are influenced by several physicochemical parameters such as pH, ionic strength and electrolyte species, temperature, solvent quality, adsorption time, and the intrinsic properties of polyelectrolytes such as charge density, concentration, architecture, and molecular weight.

Despite the several methods available for LBL assembly of multilayer films, the concept of LBL assembly based on multiple intermolecular interactions opens for a great variety of materials with well-defined properties in terms of thickness, compositions, structure, wettability, building, or charged/uncharged for a wide range of applications.

Potential applications of LbL membranes are in biomedical field such as drug delivery, gene transfection, and biosensors (Yoon et al. 2014). The controlled drug delivery can be achieved using hydrolytically degradable polymers such as poly (β -amino ester). Gene transfection is obtained by using plasmid DNA as an anionic layer to form LbL films. Biosensors can be produced by using charged biomolecules such as glucose oxidase (able to catalyze glucose oxidation with simultaneous production of hydrogen peroxide) used as glucose sensor. LbL membranes can also be used in tissue engineering by introducing functional groups onto the surface of LbL membrane able to promote cell proliferation and differentiation as substrate or by using cells as a template of LbL systems.

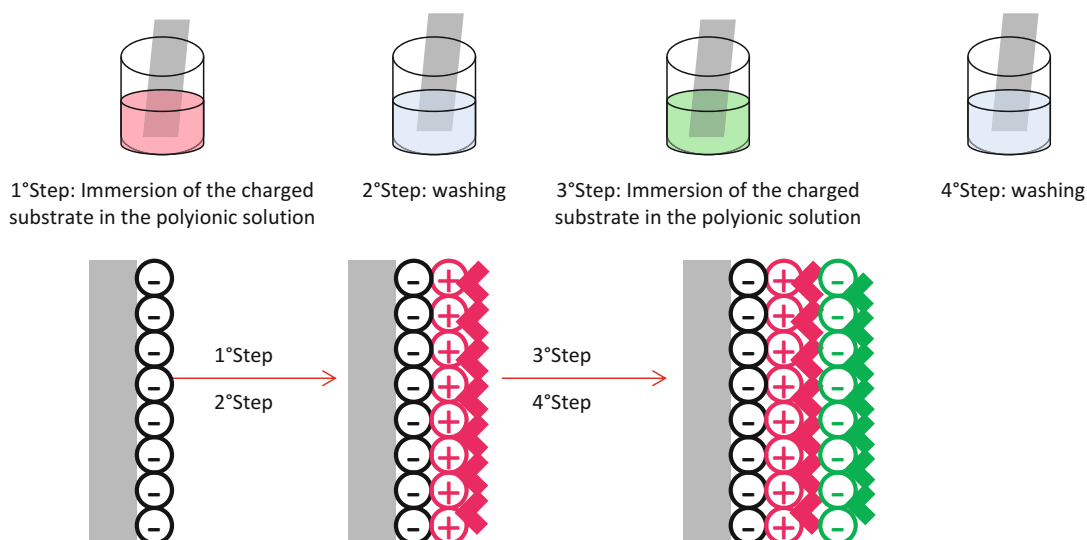
The LbL self-assembly technique has been explored in the development of electrochemical energy conversion and storage devices from fuel cells to supercapacitors (Xiang et al. 2012). Other recent applications include water treatment like water softening, desalination, and recovery of certain ions (Sanyal and Lee 2014). Advantages of LbL self-assembly technology include

- Its simplicity and low cost
- Variability of the applicable materials (conventional polyelectrolytes, water-soluble

Layer-by-Layer Self-Assembly Membrane, Table 1 Materials available for Layer-by-layer (LbL) self-assembly membranes

Molecules	Attractive Force Type	Examples
Polyelectrolyte polymers	Electrostatic interaction	Poly(styrenesulfonate) (PSS) Poly(allylamine hydrochloride) (PAH) Poly(L-lysine)/alginate (PLL/ALG) PLL/hyaluronan (PLL/HA) PLL/poly(L-glutamic acid) (PLL/PGA), PLL/poly(acrylic acid) (PLL/PAA), PGA/PAH, chitosan/HA (CHT/HA), poly(ethylenimine)/PAA (PEI/PAA)
Polymers carrying hydrogen donor and acceptor moieties	Hydrogen bonding	Poly(vinylpyrrolidone) (PVP) Poly(vinyl alcohol) (PVA) Poly(acrylamide) (PAA) Poly(ethylene oxide) (PEO) Poly(vinylpyrrolidone) (PVPON) Poly(methacrylic acid), PMAA
Uncharged molecules	Hydrophobic interactions	Alkanethiols-proteins
Molecules having complementary functional groups	Covalent bonding	Poly(vinylamine-co- <i>N</i> -vinylisobutyramide) [Poly(VAm-co-NVIBA)] and PAA. Carboxyl group of PAA activated by 1-ethyl-3-(3-(dimethylamino)propyl)-Carbodiimide hydrochloride (EDC) and amine groups of poly(vinylamine-co- <i>N</i> -vinylisobutyramide) Poly(VAm-co-NVIBA)
Stereoregular polymers carrying sites of opposite chirality	Stereocomplexation	(It-st)poly(methyl methacrylate) (PMMA)
Host (e.g., cyclodextrins, cucurbiturils, calixarenes, pillararenes, crown ethers, porphyrins) and guest (e.g., ferrocene, adamantane, azobenzene) molecules.	Host-guest interactions	Cyclodextrin (β -CD) and adamantane
Nonionic molecules, which present electron-accepting and electron-donating groups, respectively, in the side chains.	Charge-transfer interaction	Y[2-(9-carbazoyl)ethyl methacrylate] (PCzEMA, electron-donor polymer) and poly[2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate] (PDNBMA, electron-acceptor polymer)
Avidin and biotin-labeled polymers or Antibody – Antigen conjugated molecules or lectin – carbohydrate or DNA hybridization	Biologically specific interaction	Biotin – protein conjugate and polymerized streptavidin on hydrophobic silica surfaces
Metal ions and organic ligand	Coordination chemistry interactions	Poly(copper styrene 4-sulfonate) (PSS(Cu) _{1/2}), and PVP

- proteins, charged polysaccharides, as well as charged inorganic substances, including colloidal nanoparticles, heteropolyacids, and metal nanoparticles)
- Precise microstructural control and high repeatability
- Great control over the composition of the film along the vertical direction by changing the nature of the building blocks that are deposited during each step
- Extensive possibility in wide range applications
- Its nontoxic and environment-friendly nature



Layer-by-Layer Self-Assembly Membrane, Fig. 1 LbL self-assembled membranes buildup via electrostatic interactions

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Leather Industry

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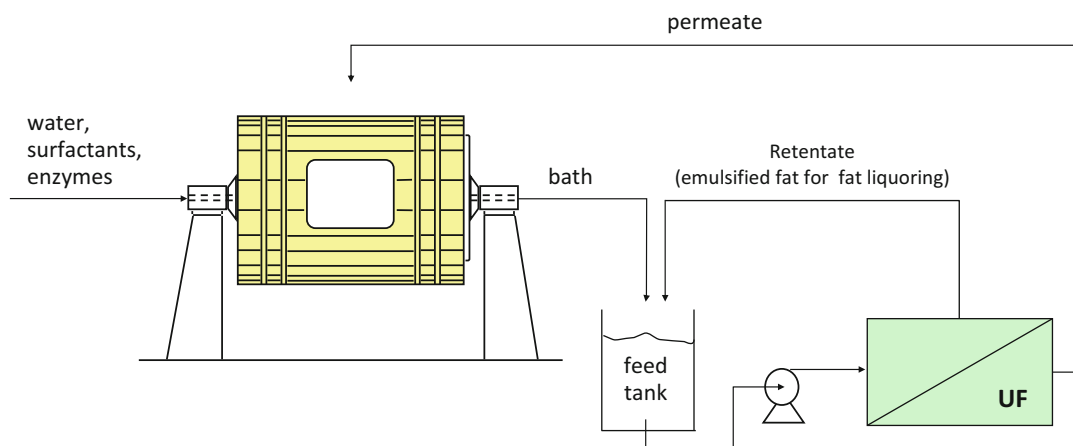
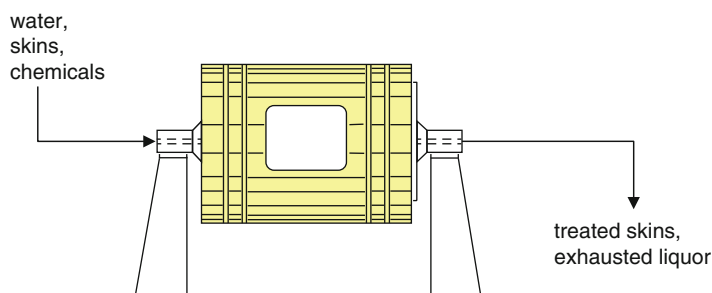
In the **leather industry**, the animal rawhide is converted into finished leather, a durable and

flexible material, through a series of chemical and mechanical treatments.

The steps in the production of leather between curing (a salt treatment to prevent putrefaction of the collagen) and tanning (a treatment of leather stabilization with vegetable or mineral substances) are collectively referred to as *beamhouse operations*. They include, in order, soaking, unhairing/liming, deliming/bating, and pickling. All these processes are realized in chemical reactors (tumblers) in which the skins react with different chemicals (acids, alkalis, chromium salts, tannins, solvents, sulfides, dyes, auxiliaries, etc.) in aqueous solutions (Fig. 1).

Wastewaters coming from different tanning operations contain high concentrations of organic and inorganic substances causing significant pollution phenomena. Organic pollutants come from the skins (it is calculated that the raw skin has 30 % loss of organic material during the working cycle), or they are introduced during the working cycle (e.g., tanning). Inorganic pollutants are a residual of the used chemicals (i.e., chromium salts) that are not completely fixed by the skins owing to the low efficiency of the operations (Cassano et al. 2001).

Leather Industry,
Fig. 1 Scheme of tumbler



Leather Industry, Degreasing, Fig. 1 Scheme of aqueous degreasing combined with ultrafiltration process

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Leather Industry, Degreasing

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In the degreasing step, fats and grease are removed from the interfibrillary spaces with the use of lipases, detergents, or solvents in order to

allow the penetration of various tanning materials and dyes. This operation is necessary especially for sheepskins where the percentage of fat substances on raw weight is of about 30–40 %.

Enzymatic degreasing is a better way of carrying out degreasing than the use of solvents and detergents. Lipases are much safer and less toxic to workers and the environment.

Ultrafiltration (UF) can be used to treat the exhausted bath from the degreasing operation in order to recover surfactants in the permeate stream which can be recycled to the degreasing step leading to a reduction in raw material costs. Fat substances removed from the skins can be concentrated in the retentate stream and reused, after physical and chemical treatments, in the fat liquoring step with significant reduction of the wastewater treatment costs (Koltuniewicz 2010).

In another approach the UF process can be combined to an enzymatic degreasing step (Fig. 1) with a continuous recycling of the permeate stream in the drum (Cassano et al. 1998).

The proposed methodology permits to obtain a high removal efficiency of fatty substances from the degreasing bath and a reduction of washing cycles normally employed to remove the lipidic substances from skins and, consequently, of water consumption. Polysulfone membranes with molecular weight cutoff of 20 kDa, in spiral-wound configuration, exhibited rejections toward chemical oxygen demand (COD) and fat substances higher than 97 %.

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Leather Industry, Soaking

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In this operation, raw skins are exposed to water and chemicals (small quantities of imbibing substances) in order to hydrate proteins and fibers, to solubilize the denatured proteins, and to eliminate

salt compounds with dirt (blood, excrement, earth) which are attached to the skins.

The soaking-exhausted effluent-containing excrements, salts, and chemical additives are normally discharged into a water-treatment plant (Sharphouse 1983).

UF membranes can be used to concentrate organic components in the feed tank of the UF plant. A clear permeate, enriched in salt compounds, could be reused in the pickling step after adjustment of the salt concentration with NaCl (Fig. 1). Preliminary treatments are necessary in order to remove the suspended materials; a sedimentation step allows to reduce the suspended solids of 90 %; then steel spring filters (200–300 μm net size) could be employed to remove large particles avoiding clogging phenomena of UF membranes (Cassano et al. 2001).

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Leather Industry, Unhairing-Liming

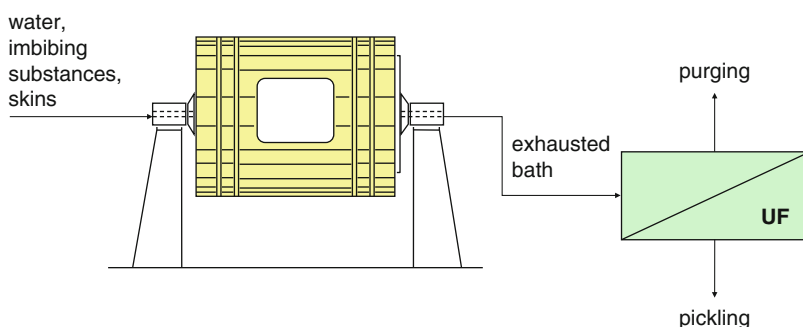
Alfredo Cassano

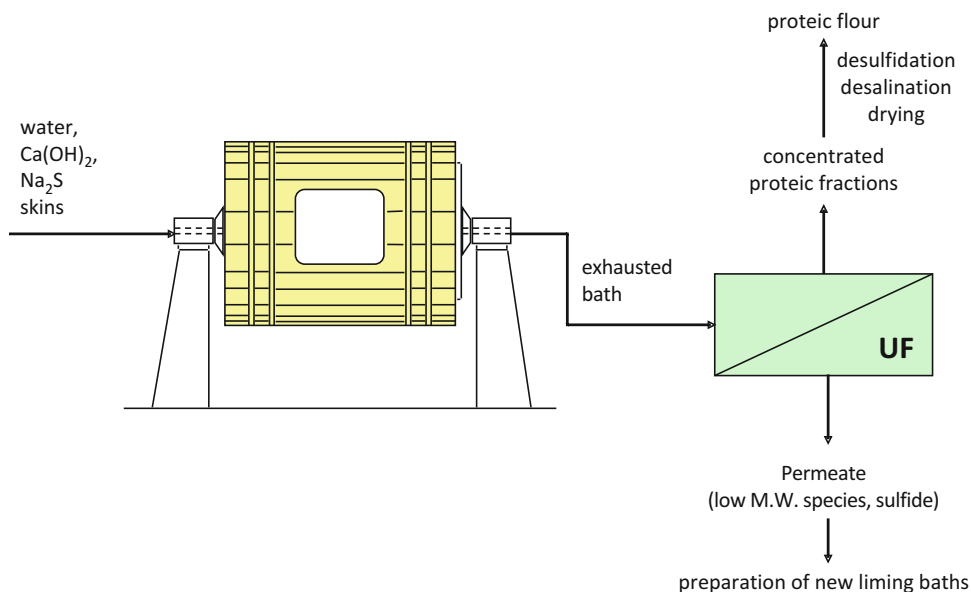
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The aim of the unhairing-liming step is to remove from the raw skin all the components which are

Leather Industry, Soaking,

Fig. 1 Treatment of exhausted effluents of the soaking step by UF process





Leather Industry, Unhairing-Liming, Fig. 1 Treatment of exhausted liming effluent by ultrafiltration

not transformed into leather, such as the superficial epidermis including the hair and the subcutaneous adipose layer. The liming step introduces chemicals such as lime (Ca(OH)_2) and sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS) which open the fibrous structure of the skin. Consequently, exhausted effluents are highly polluted for the presence of sulfide, amines, organic matter coming from degradation of hairs and epidermis, and high concentration of alkalis. The COD of exhausted effluents ranges between 20,000 and 40,000 mg/L of consumed oxygen.

The UF treatment of the exhausted unhairing liquor has been one of the first membrane approaches introduced in the leather industry (Molinari 1995). It can be exploited to recover sulfide and solubilized lime together with low molecular weight proteic substances in the permeate stream in order to reuse the purified solution for the preparation of a new liming bath. High molecular weight proteic components, coming from chemical degradation of hairs and epidermis, are concentrated in the retentate stream (Fig. 1).

Considering that 60–65 % of the initial sulfide remains in the exhausted liquor and 5–10 % is lost in the retentate, the quantity of sulfide that is possible to recycle with an UF system is 55–60 %.

An innovating system based on the use of enzymes and small quantities of sodium sulfide (1.5 % instead of 10 %) has been proposed and tested on industrial scale. In this approach the enzymatic unhairing was combined to the continuous cross-flow UF of the bath permitting to keep constant the sulfide concentration in the unhairing bath due to its permeation through the UF membrane. The organic components (products of degradation of the keratin and of the interfibrillar proteins, fat substances, etc.) are concentrated in the retentate stream. This new approach is safer for workers and characterized by a reduced environmental impact because hairs are not dissolved and can be removed separately (Cassano et al. 1998).

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Leather Processing, Chromium Recovery

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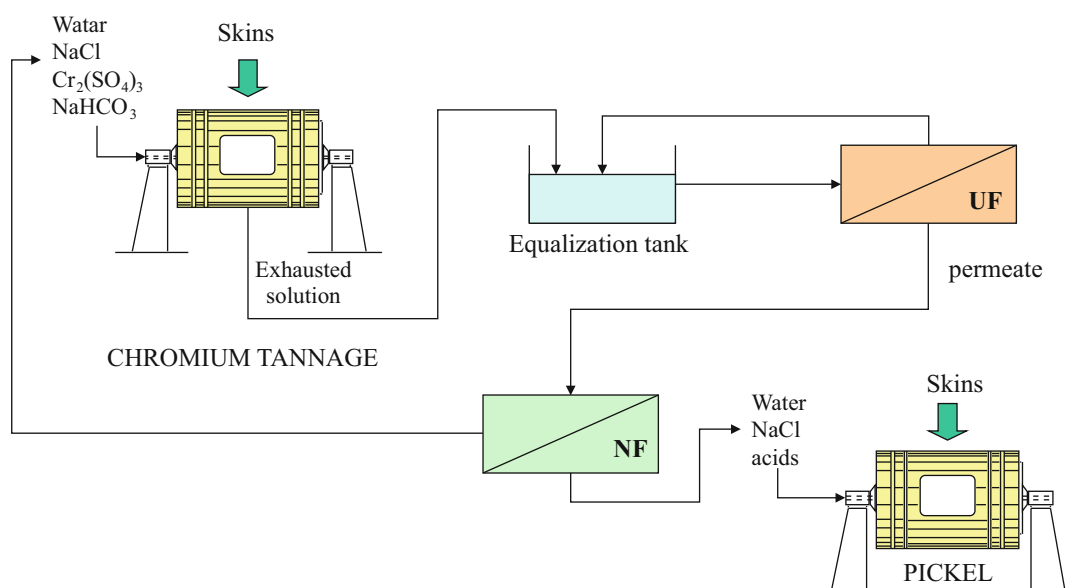
In the tannage operation tanning agents are used in order to prevent the leather from chemical and thermal degradation. The most common tanning agent is the chromium basic sulfate. It enters the pores of the skin by a diffusion process to react with the collagen carboxyl groups and to form inter- and intramolecular cross-linking which results in physical, chemical, and biological stability.

The exhausted bath coming from the chromium tannage contains about 30 % of the

initial salt content and it is normally sent to a cleaning-up plant. Here chromium salts end up into the sludges creating serious problems for their disposal.

Chromium recovery from tanning exhausted baths represents a significant economical advantage for the leather industry in terms of its reuse and for the simplification of the depolluting process of global effluents.

An integrated process based on a preliminary ultrafiltration (UF) of the spent liquor followed by a nanofiltration (NF) treatment of the UF permeate has been proposed as a technically viable method for recovering chromium salts from spent tanning liquors (Cassano et al. 1996, 2007). The UF process allows a marked reduction of suspended solids and fat substances. The concentrated chromium solution obtained in the NF process can be reused for the preparation of new tanning baths. The NF permeate can be reused in the pickling step because of its high content of chlorides (Fig. 1).



Leather Processing, Chromium Recovery, Fig. 1 Proposed process scheme for the chromium recovery from exhausted chromium baths

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Leather Processing, Deliming-Bating

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The deliming step is carried out to reduce the excess of liming agents used in the previous unhairing operation by using acids and/or acidic salts. Since the pH must be slowly lowered, ammonium salts are commonly used for this purpose. In the bating operation, skins are treated with proteolytic enzymes in order to open the fibrous structure of skins, increasing their softness.

Generally, deliming and bating operations are performed in the same drum. Wastewaters from these operations are characterized by high nitrogen content, coming from both the hide structure

and from the ammonium sulfate used as chemical auxiliary.

In order to reduce the nitrogen concentration in the deliming/bating exhausted bath, the replacement of ammonium salts by carbon dioxide (CO₂) and the reuse of wastewater and chemicals after membrane filtration (MF or UF) of the exhausted liquor has been proposed (Gallego-Molina et al. 2013).

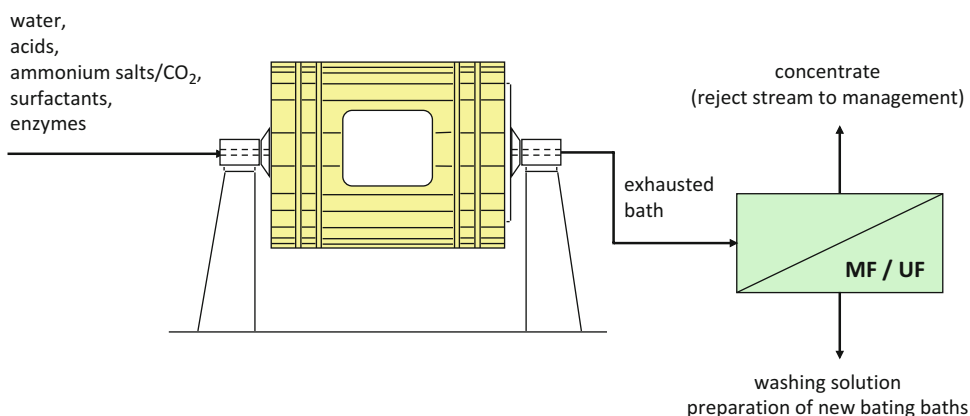
MF or UF membranes lead to a remarkable reduction of COD and fat substances of the exhausted liquor (Cassano et al. 2001). The permeate solution can be reused for the preparation of new bating baths or as washing water (Fig. 1), providing environmental and economic benefits due to the water consumption reduction and the reduction in nitrogen and salt discharge.

Cross-References

- [Durability of Membrane \(Lifetime of Membrane\)](#)

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Leather Processing, Deliming-Bating, Fig. 1 Proposed process scheme for the treatment of exhausted deliming baths

Lipid Coverage of a Regenerated Cellulose Membrane: Effect on Ion Transport

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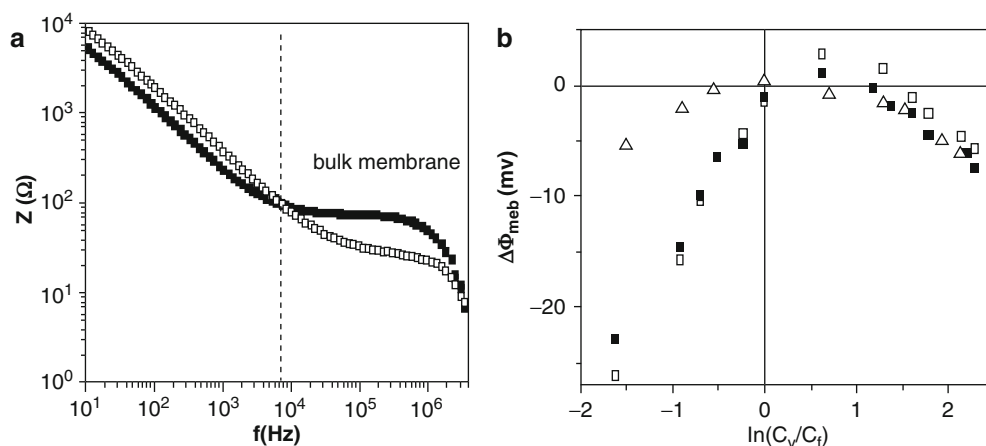
The modification of solid substrates and membranes using biomaterials is an attractive field of research for developing new devices such as biosensors, structured multilayers, biomembrane mimetics, biomaterial coatings for therapeutical applications, etc. (Goodsell 2004; Sackmann 1996). Particularly, lipid-layer deposition on membrane supports might improve their biocompatibility, but it might also affect membrane transport parameters and, consequently, its functionality.

Changes in electrical and transport parameters for a hydrophilic regenerated cellulose membrane (RC sample) as a result of lipid surface deposition (RC/LL sample) were studied by measuring impedance spectroscopy (IS) and membrane potential. Lipid-layer (glyceryl tristearate as main lipid with L- α -phosphatidylcholine and sodium taurocholate as surfactants) deposition

on RC supports was already described (Benavente et al. 2011).

Impedance is an a.c. technique for determining membrane electrical resistance and capacitance by measurements performed at different frequencies (Benavente 2009). As was already indicated (Benavente et al. 2011), IS measurements for dry LL-modified membranes showed a reduction in conductivity and dielectric constant when compared with original regenerated cellulose support, estimating a thickness of ~ 2 nm for the LL. Figure 1a shows a comparison of Z vs frequency plots for hydrated RC and lipid-layer RC/LL membranes, where differences associated with electrode-membrane interface ($f < 5$ kHz) and bulk membrane can be observed as an indication of lipid coverage of RC support and its effect on the reduction of water (or electrolyte) adsorption by the cellulose structure.

Membrane potential ($\Delta\phi_{\text{meb}}$) is the electrical potential at both sides of membranes in contact with different electrolyte concentrations, and Fig. 1b shows $\Delta\phi_{\text{meb}}$ values vs NaCl concentration ratio c_v/c_c . Two different $\Delta\phi_{\text{meb}} - \ln(c_v/c_c)$ relationships are observed depending on the concentration ratio values: (i) a Donnan-potential contribution for $0.2 \leq c_v/c_c \leq 10$, which is associated with co-ion (Cl^-) exclusion due to the weak membrane effective charge ($X_{\text{ef}} \sim -0.009$ M);



Lipid Coverage of a Regenerated Cellulose Membrane: Effect on Ion Transport, Fig. 1 (a) Impedance plot. (b) Membrane potential dependence on NaCl concentration ratio. RC ($\square$), RC/LL ($\blacksquare$), and FTC ($\triangle$)

(ii) when $2 > c_v/c_c > 10$, the higher contribution seems to correspond to the diffusion potentials as a result of the different transport of counterions (t_+) and co-ions (t_-) in the membrane. Lipid layer does not seem to affect membrane fixed charge, according to the similar $\Delta\phi_{meb}$ values obtained with RC and RC/LL membranes for the Donnan-potential branch (i), but differences in ion transport number should exist due to their different diffusion-potential contribution ($\langle t_+^{RC} \rangle = 0.74$, $\langle t_+^{RC/LL} \rangle = 0.69$) (ii). For comparison, $\Delta\phi_{mbr}$ values for tomato fruit cutin (FTC), a membrane with lipids as major component (Heredia-Guerrero et al. 2012), are also drawn in Fig. 1b, and its comparison with RC/LL results indicates lower fixed charge ($X_f^{FTC} \approx -510$ – 4 M) but rather similar transport parameters ($\langle t_+^{FTC} \rangle = 0.68$) supporting the reliability of RC/LL values.

These results show small changes in transport parameters associated with LL deposition and open the scope to study natural membranes.

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Lipid Monolayer/Bilayer

► Amphiphilic Membrane

Lipids/Phospholipids

► Amphiphilic Molecules

Liquid Chromatography: Organic Carbon Detection (LC-OCD)

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Liquid chromatography – organic carbon detection (LC-OCD) is an analytical technique for identification and quantification of natural organic matter (NOM) constituents in aquatic environments and water-soluble synthetic organic matter in technical waters. This technique has several specific applications including NOM investigation in drinking water, wastewater, and marine waters and quality control monitoring of ultrapure water used in power plants and the semiconductor industry (Huber and Frimmel 1994; Huber et al. 2011). It is widely applied in membrane-based water treatment to characterize the different NOM constituents in the source waters (e.g., Kennedy et al. 2005; Amy et al. 2011; Villacorte et al. 2012), to assess the organic removal efficiency of pretreatment and membrane filtration processes (e.g., Frimmel et al. 2004; Villacorte et al. 2009, 2010; Huang et al. 2011; Zheng et al. 2010), and to identify the NOM constituents that cause fouling in MF/UF and NF/RO systems (e.g., Huber 1998; Henderson et al. 2011; Kennedy et al. 2008; Jiang et al. 2010; Batsch et al. 2005; Zheng et al. 2009).

The principle behind NOM fractionation by LC-OCD is based on three separation processes, namely, size exclusion, ion interaction, and

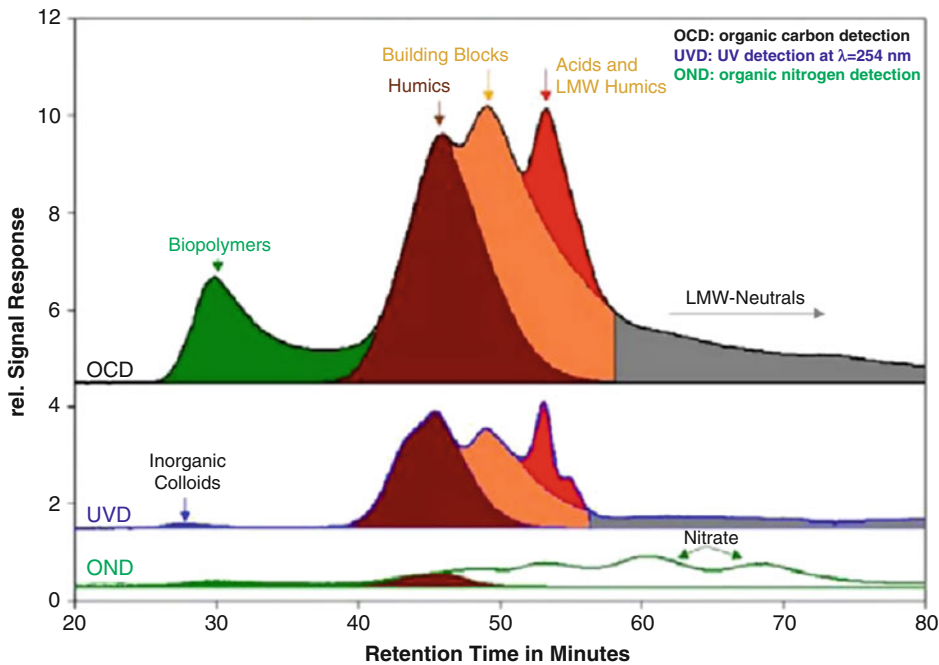
hydrophobic interaction. Since NOM constituents are highly heterogeneous in terms of size and majority of which are hydrophilic and weakly acidic, size exclusion is considered as the dominant mechanism of separation (DOC-Labor 2006). Size exclusion chromatography (SEC) is

based on steric interactions or physical sieving where the difference in speed of diffusion for smaller and larger molecules is used to identify the different NOM fractions in the mobile phase (e.g., buffered water sample). The stationary phase is a packing of porous beads which allows smaller molecules to diffuse into the bead interior while preventing the larger molecules to diffuse through. As a consequence, larger molecules have less volume to traverse and travel faster through the chromatogram column (shorter elution time) than smaller molecules.

Liquid Chromatography: Organic Carbon Detection (LC-OCD), Table 1 Characteristics of different constituents of NOM identifiable by LC-OCD (www.doc-labor.de; Huber et al. 2011; Batsch et al. 2005)

NOM fraction	Typical size (Da)	Typical composition
Biopolymers	>20,000	Polysaccharides, proteins, amino sugars, polypeptides, TEPs, EPS
Aquatic humics	~1000	Humic and fulvic acids
Building blocks	300–450	Weathering and oxidation products of humics
LMW neutrals	<350	Mono-oligosaccharides, alcohols, aldehydes, ketones, amino acids
LMW acids	<350	All monoprotic organic acids

The modern LC-OCD technology is mainly attributed to the works of Stefan Huber in the early 1990s when he successfully improved the sensitivity of the LC/DOC (predecessor of LC-OCD) developed earlier at the Engler-Bunte Institute in Karlsruhe, Germany (http://www.doc-labor.de/). The current LC-OCD system has an online organic carbon detector (OCD), UV detector (UVD), and organic nitrogen detector (OND) to continuously measure the relative signal response of organic carbon, UV, and organic nitrogen, respectively, at different retention



Liquid Chromatography: Organic Carbon Detection (LC-OCD), Fig. 1 Typical LC-OCD chromatogram of NOM in surface water (DOC-Labor 2006)

times. In principle, the analysis technique is as follows: (1) injection of buffered particle-free water sample to a chromatographic column to separate fractions of NOM, (2) nondestructive UV detection at 254 nm wavelength, (3) organic carbon detection based on high-sensitivity TOC analysis, and (4) simultaneous detection of organic nitrogen in bypassed samples after the UV detector (see detailed specifications by Huber et al. 2011). The chromatogram data generated by the three detectors are processed using a customized software program (ChromCALC, DOC-Labor, Karlsruhe) to calculate organic carbon concentrations of biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and neutrals fractions of NOM based on area integration of the fractional peaks. The lower limit of detection of this technique was reported to be in the low-ppb range for individual fractions (Huber and Frimmel 1991). The typical size ranges and chromatograms of the different NOM fractions detectable by LC-OCD are shown in Table 1 and Fig. 1, respectively.

Cross-References

- Extracellular Polymeric Substance (EPS)
- Natural Organic Matter (NOM)
- Transparent Exopolymer Particle

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Liquid Crystal Polymer Membranes

P. C. van H. Kuringen, A. P. H. J. Schenning and D. J. Broer

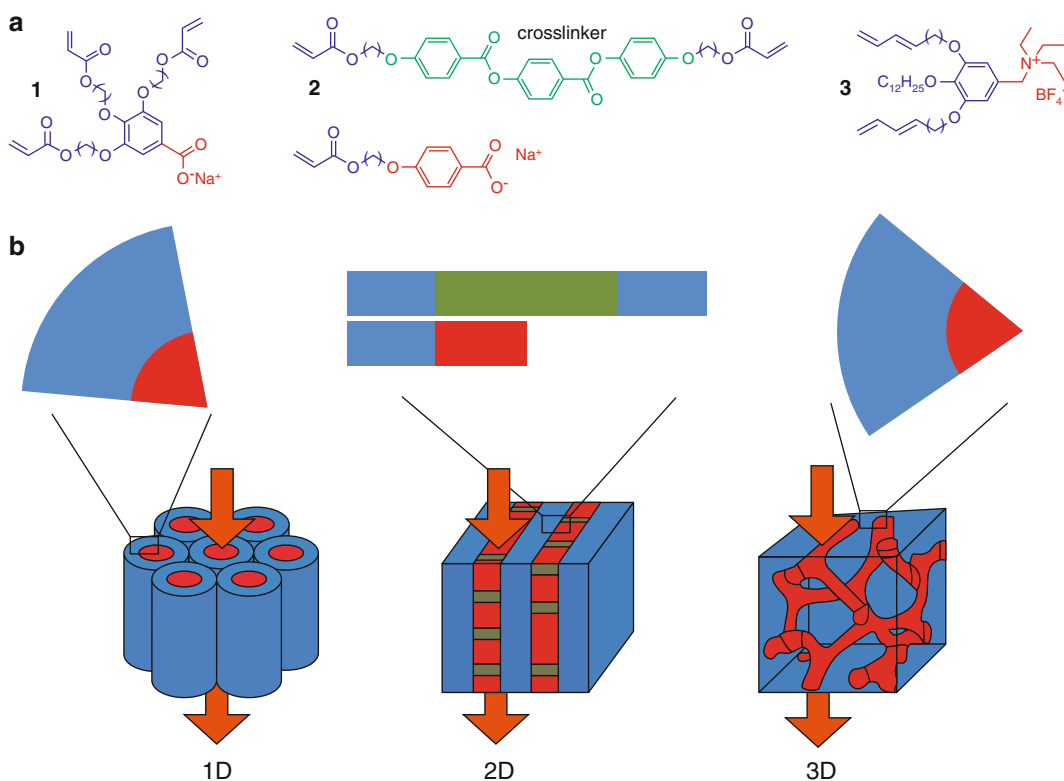
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Liquid crystals (LCs) combine properties of both liquids and crystals and can be organized in a variety of nanostructured polymer films with a monolithic structure. Therefore, polymer-based LCs are ultimately suited as membrane with an accurately controlled nanoporosity. Nanoporous

membranes that have a large surface area to volume ratio are of great current interest for their potential application in filtration, separation, ion conductivity, drug delivery, and catalysis. The small pore size in these materials (less than 1 nm) makes discrimination between molecules and ions based on size and shape possible.

LCs can self-assemble in a variety of phases that have orientation order and, in some cases, positional order. For the construction of nanoporous membranes, various phases have been used. Well-known examples are hexagonal or columnar, lamellar or smectic, and cubic phases (Fig. 1).

One-dimensional pores are made from LCs with either a hexagonal or a columnar phase. These phases are assumed by disk-shaped LCs: the polar regions are located at the center of the



Liquid Crystal Polymer Membranes, Fig. 1 (a) Examples of chemical structures of the LCs used in the construction of nanoporous membranes. One columnar or hexagonal LC, two smectic or lamellar LC, and three bicontinuous cubic LC. (b) The self-assembly of these

materials to form nanostructured materials, with respectively one, two, or three dimensional pores. The red part represents the pore while the blue fraction is the molecular region (Adapted with permission from reference (Kato 2010). Copyright Wiley, VCH)

columns and the hydrocarbon tails form the surrounding matrix (Fig. 1-a1). If the molecules are well aligned, these one-dimensional pores are interesting for their low tortuosity. The straight pores result in a short path length through the thickness of the material. The cylindrical pores must be continuous through the membrane and uniformly aligned perpendicular to the film surface for optimum transport.

Two-dimensional pores can be created by smectic LCs (Fig. 1-a2). These rod-like LCs self-assemble in lamellar-like structures where the molecules are orientated perpendicular to the layers. A lamellar structure is created with alternating layers of a two-dimensional polymer sheets and two-dimensional pores. However, these sheets do not connect to each other. To circumvent disruption of the film, crosslinkers are used to keep the layers together. To some extent the pore size of the materials can be controlled by the length of the crosslinker.

A bicontinuous cubic phase is used to make nanostructured LC membranes with pores in three dimensions (Fig. 1-a3). Generally, the molecular structure of the LC differs only slightly from the LCs used for the columnar phase. However, the self-assembly is different. Now, no alignment of the pores is needed, since the pores are orientated in three dimensions.

These nanostructured LC polymer networks are used for different membrane applications, such as (anisotropic) ion conductivity (Schenning et al. 2011; Kato 2010) and gas separation (Schenning et al. 2011; Gin et al. 2006). Permeation is the product of diffusion and solubility. Therefore the solubility values of the ions and gases are very important. The local organization of the nanostructured material can promote the solubility of certain species, whereas other molecules are less soluble. This results in higher permeation and selectivity of the desired molecules compared to isotropic material of the same composition. Another application is the nanofiltration of water (Schenning et al. 2011; Gin et al. 2006; Henmi et al. 2012). Molecules smaller than the pore size can pass through the membrane, while

larger molecules (contaminants) are rejected. The presence of charges in the pores of the membranes enables the selective permeation (Gin et al. 2006; Henmi et al. 2012) of ions with a remarkable selectivity: for example, a membrane with pore size of approximately 0.6 nm was shown to transport more divalent sulfate ions than monovalent chloride ions (Henmi et al. 2012). Furthermore, the pore size can be tailored to control the passage of molecules, making them suitable for programmed drug release systems or the confined environment within the material can be used to enhance chemical reactions.

Nanoporous LC polymer membranes can be produced with pore sizes of 1 nm and below. Unique features can be realized, but because of the length of the pores exceeding micrometers, the permeability of liquids is generally low with high pressures necessary to achieve sufficient flow across the membrane. The challenge in this field is to make thinner membrane films of a mechanically robust material that can withstand these high pressures. Research on using mesoporous supporting layers to endure the force while the LC polymer membrane determines the separation characteristics is being undertaken.

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Liquid Entry Pressure (LEP or LEPW)

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In membrane distillation it is of paramount importance that liquid does not fill the membrane pores, in order to keep membrane efficiency to the highest possible value. To this end hydrophobic membranes are normally used. The hydrophobicity can be quantified through the so-called liquid entry pressure (LEP) parameter, defined as the pressure difference at which liquid penetrates into the membranes pores.

The pressure required to force water through the structure is inversely proportional to the opening size and dependent on the polymeric properties of the membrane. A theoretical expression, based on Young-Laplace equation, enables the estimation of LEP (see, e.g., El Bourawi et al. 2006):

$$\Delta P = \frac{2\gamma \cos\theta}{r}$$

where γ is the liquid surface tension, θ the contact angle between liquid and membrane, and r is the pore radius.

Given the practical difficulty of obtaining the exact value of the above physical parameters, it is not uncommon to estimate LEP experimentally, and Smolders and Franken (1989) described a detailed procedure which should be followed in this case. Basically pressure difference is gradually applied on both side of the membrane until the first drop of the liquid appears on the permeate side (more specific description is given in the suggested reference). Typical values of LEP range from tenth to tens of bars (0.1–20 bar): for example, with liquid water at ambient condition, a PTFE membrane with 95 % porosity, 25 μm thickness, and 3 μm nominal pore size has an LEP of 0.13 bar, whereas a PTFE supported membrane with 75 % porosity, 120 μm thickness, and 0.2 nominal pore size has an LEP of 4.0 bar (Kim and Harriot 1987).

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Liquid Membrane Separation

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Liquid membrane separation combines the solvent extraction and stripping processes (re-extraction) in a single step.

This entry has the objective of introducing the reader to the basic definitions of the liquid membrane field, with classification.

The term liquid membrane transport includes processes incorporating liquid-liquid extraction (LLX) and membrane separation in one continuously operating device. It utilizes an extracting reagent solution, immiscible with water, stagnant or flowing between two aqueous solutions (or gases), the source or feed, and receiving or strip phases. In most cases, the source and receiving phases are aqueous, and the membrane is organic, but the reverse configuration can also be used. A polymeric or inorganic microporous support (membrane) may be used as bearer (as in SLM) or barrier (as in BLM technologies) or not used, as in ELM and layered BLM (see respective entries: SLM, ► [Emulsion Liquid Membrane \(ELM\)](#), ► [Silver Recovery by Bulk Liquid Membrane \(BLM\)](#)).

The great potential for energy saving, low capital and operating cost, and the possibility to use expensive extractants, due to the small amounts of the membrane phase, make LMs an area deserving special attention. Liquid membrane systems

are being studied extensively by researchers in such fields as analytical, inorganic, and organic chemistry; chemical engineering, biotechnology, and biomedical engineering; and wastewater treatment. Research and development activities within these disciplines involve diverse applications of liquid membrane technology, such as gas separations, recovery of valued or toxic metals, removal of organic compounds, development of sensing devices, recovery of fermentation products, and some other biological systems.

The general properties of liquid membrane systems have been a subject of extensive theoretical and experimental studies. Some general characteristics of LM processes are as follows:

1. Liquid membrane separation is a rate process, and the separation occurs due to a chemical potential gradient, not by equilibrium between phases.
2. LM is defined based on its function, not the material used in fabrication.

Permeation is a general term for the concentration-driven membrane-based mass transport process. Differences in the permeability produce a separation between solutes at constant driving force. Because the diffusion coefficients in liquids are typically orders of magnitude higher than in polymers, a larger flux can be obtained with liquid membranes. Application of a pressure difference, an electric field, or temperature considerably intensifies the process.

There are several different directions in LM separation classifications: according to module design configurations (see SLM, ► [Emulsion Liquid Membrane \(ELM\)](#), ► [Silver Recovery by Bulk Liquid Membrane \(BLM\)](#) entries), according to transport mechanisms (see ► [Transport Mechanisms with Liquid Membranes](#)), according to applications, according to carrier type, and according to membrane support type. Below, these types of classifications are described and discussed briefly.

According to configuration definition, three groups of liquid membranes are usually

considered (see Fig. 1): bulk (BLM), supported or immobilized (SLM or ILM), and emulsion (ELM) liquid membrane transport. Some authors add to these definitions polymeric inclusion membranes, gel membranes, and dual-module hollow-fiber membranes, but, to my opinion, the first two types are the modifications of the SLM, and the third is the modification of BLM.

According to the transport mechanisms, the LM techniques may be divided into simple transport, facilitated or carrier-mediated transport, coupled counter- or cotransport, and active transport.

According to applications, the LM techniques may be divided into (1) metal separation-concentration, (2) biotechnological product recovery-separation, (3) pharmaceutical product recovery-separation, (4) organic compound separation and organic pollutant recovery from wastewaters, (5) gas separations, (6) fermentation or enzymatic conversion-recovery-separation (bioreactors), (7) analytical applications, and (8) wastewater treatment including biodegradation-separation techniques.

Classification according to carrier type is as follows: (1) water-immiscible, organic carriers, (2) water-soluble polymers, (3) electrostatic, ion-exchange carriers, and (4) neutral, but polarizable carriers.

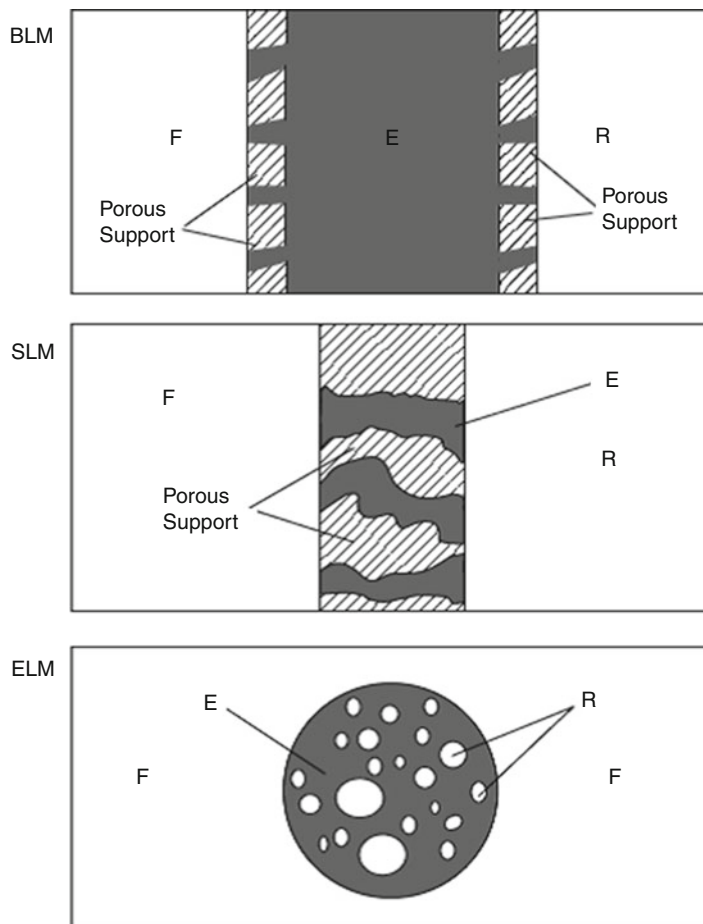
Classification according to membrane support type is as follows: (1) neutral hydrophobic, hydrophilic membranes, (2) charged (ion-exchange) membranes, (3) flat sheet, spiral module membranes, (4) hollow-fiber membranes, and (5) capillary hollow-fiber membranes.

Module design configurations are used as a rule as basic classification.

Practically, there are a lot of opportunities for liquid membrane separation processes in many areas of industry. The most interesting developments for industrial membrane technologies are related to the possibility of integrating various membrane operations in the same industrial cycle, with overall important benefits in terms of product quality and plant compactness.

Liquid Membrane

Separation, Fig. 1 Three configurations of liquid membrane systems: bulk (BLM), supported (immobilized) (SLM or ILM), and emulsion (ELM). F is the source or feed phase, E is the liquid membrane, and R is the receiving phase

**Liquid Permeability**

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Liquid permeability is a liquid flux normalized by driving force – applied pressure difference across the membrane. Liquid permeability can be expressed in volumetric or gravimetric units – $[l/(m^2 \cdot h \cdot bar)]$ or $[kg/(m^2 \cdot h \cdot bar)]$, respectively. This parameter is used to characterize the membrane productivity and passage of pure solvent or solution, in liquid separation process such

as micro-, ultra-, and nanofiltration, reverse and forward osmosis, or hybrid processes like membranes for fuel cell. For commercial membranes liquid permeability is usually given by manufacturers along with value of molecular weight cutoff (MWCO); the last one is characterized the ability of the membrane to reject the solutes with certain molecular weight. Since it is already normalized by driving force of the process, liquid permeability shall be most likely constant value for specific membrane in certain range of operated pressures at constant feed composition and temperature. Due to its uniformity, this parameter allows to compare performance of diverse number of membranes between each other, tested in accordance with different filtration protocols.

In some cases, the liquid permeability can be a function of transmembrane pressure, especially if the membrane material of top layer has a noticeable affinity to the solvent like for organic solvent nanofiltration. Then, increase of pressure difference across the membrane could lead to partial compaction of swollen polymer matrix resulting in some decline of liquid permeability (Volkov et al. 2008). This is typically a reversible effect, and the membrane recovers its transport properties, while the pressure is reduced again. However, if it is accompanied by collapsing of the membrane porous structure or transformation of membrane morphology (e.g., as a result of chemical cleaning), the change in liquid permeability is irreversible. In a case of membrane fouling, there could be a combination of reversible and irreversible decline in liquid permeability, and partial recovery of membrane performance is possible after regeneration stage (Drioli and Giorno 2010).

Liquid permeability can be determined from filtration experiments in dead-end or cross-flow regimes. Ideally, no difference between two regimes shall be expected for filtration of pure solvents or dilute solutions of solutes with no specific interaction with membrane material. Meanwhile, it is preferable to carry out the filtration test in cross-flow membrane cell with high linear velocity in order to minimize concentration polarization effect or membrane fouling during the filtration of real mixtures (e.g., ground or wastewater).

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Liquid-Liquid Membrane Extraction

► Membrane Based Solvent Extraction

Lotus Effect

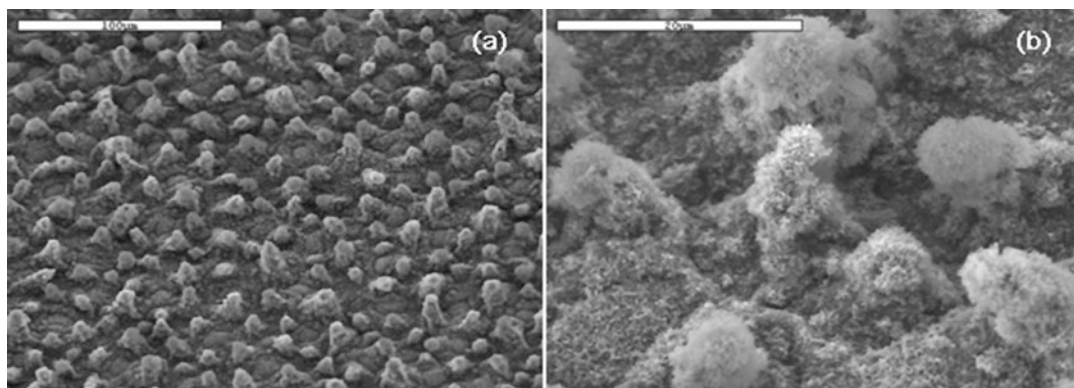
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Lotus leaf (*Nelumbo nucifera*) has become the epitome of natural superhydrophobic surfaces and has long been considered as a sacred symbol of purity for thousand years in oriental culture due to its impressive self-cleaning feature, where leaves remain unsmudged even being immersed into muddy water. Water contact angle on lotus leaf is reported above 160° with few degrees of roll-off angle. Therefore, *lotus effect* is sometimes a synonym for superhydrophobicity or self-cleaning nowadays. Although the effect has long been noticed for several generations, a systematically detailed investigation was not carried out until 1997 where more than 200 water-repellent plants were studied via scanning electron microscopy (Neinhuis and Barthlott 1997). The study reveals the secret of lotus leaf, which, not surprisingly, attributes to its combination of surface roughness and chemical substances. Hydrophobicity and self-cleaning of lotus leaf are believed as a mechanism to resist harmful microorganism bounding to the leaf surface, since water is usually required for the germination.

The lotus leaf is covered by small protrusions (Fig. 1a) called papillae with their average diameter and height about 10 μm. The papillae are further covered by an additional layer of epicuticular waxes, generated from epidermal cells (Fig. 1b). These wax crystals are presented in submicron size and in crystalline tubules with water contact angles of about 95–110°, which is considered hydrophobic. The epicuticular waxes play a practically important role as they are not only to provide hydrophobicity but to generate an additional roughness in a smaller length of scale other than micron-sized bumps. The absence of wax crystals, i.e., dropping hot water onto the leaf, will totally eliminate the superhydrophobicity (Liu et al. 2009). The



Lotus Effect, Fig. 1 SEM micrographs of lotus leaf showing its relatively rough surface covered by small micron-sized protrusions (a) and submicron-sized wax crystals (b) (Hsu 2010)

kind of hierarchical roughness on superhydrophobic surfaces seems to play a crucial role, but the detailed mechanism is not yet completely clear. A general benefit suggested is to repel both macro- and micro-scope water droplets (Nosonovsky and Bhushan 2007). Surfaces with only one scale of roughness repelled macroscopic droplets fairly well, while the condensation may easily form microscopic droplets between the grooves of the surface structure.

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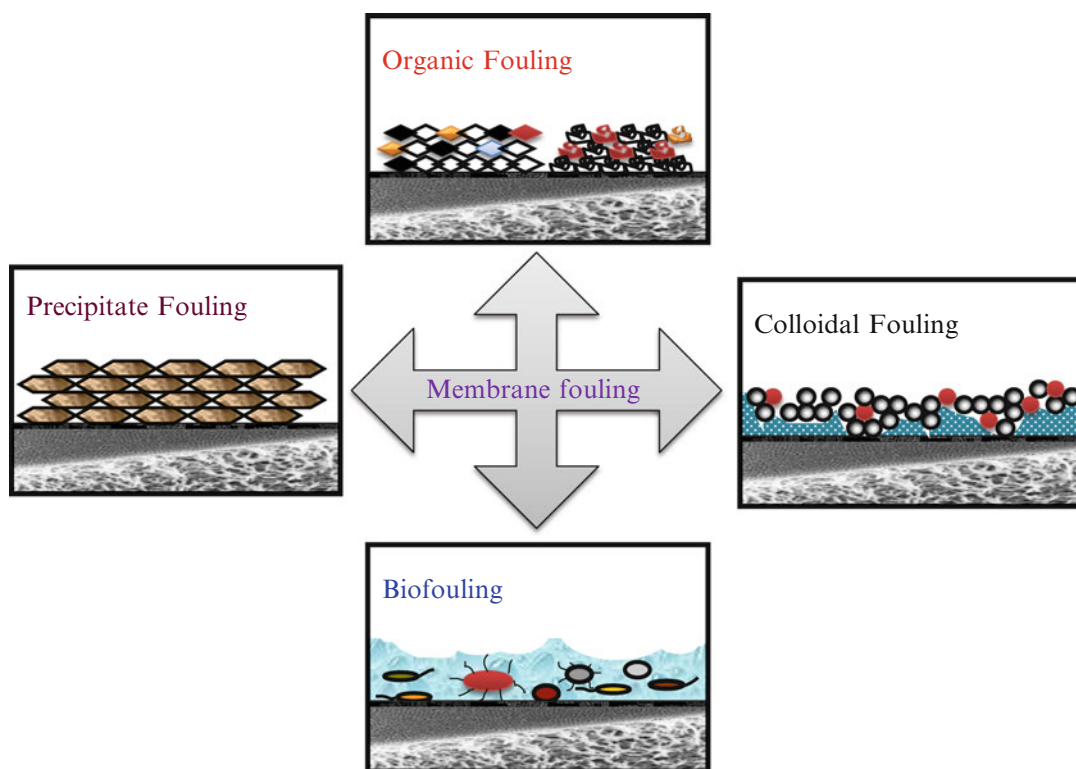
Low Fouling Membranes

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Membrane fouling – a common hindrance to the advancement of water treatment and

separation membrane technologies, including microfiltration, ultrafiltration, nanofiltration, and osmosis processes – diminishes process productivity, raises operating costs, and shortens membrane life span. Fouling is the deposition of retained particles, colloids, macromolecules, salts, etc., at the membrane surface or inside the pore, and at the pore walls. Fouling reduces the membrane flux either temporarily or permanently. The decrease of permeate flux or irreversible membrane fouling is recognized as the main problem in the application of membrane filtration technologies. Several types of membrane fouling have been introduced including inorganic fouling or scaling, colloidal fouling, organic fouling, and biofouling. A schematic representation is given in Fig. 1. Among them, the formation of biofilms on the membrane surfaces or membrane biofouling has been regarded as the most serious problem. The biofouling or biofilm formation starts with the adsorption of proteins and humic substances on membrane surfaces which serves as nutrient for microorganisms (Banerjee et al. 2011; Lejars et al. 2012). The two major approaches to combat surface fouling are based on either preventing foulants from attaching or degrading them. It is generally accepted that an increase in hydrophilicity offers better fouling resistance because protein and many other foulants are hydrophobic in nature (Rana and Matsuura 2010). The high hydrophilicity leads to a high surface hydration which is generally considered



Low Fouling Membranes, Fig. 1 Schematic representation of different types of fouling

the key to nonspecific protein adsorption resistance, organic fouling, microorganisms attachment, etc., since a tightly bound water layer forms a physical and energetic barrier to prevent the adsorption to the surface. While protein-resistant coatings may also resist bacterial attachment and subsequent biofilm formation, in order to overcome the fouling-mediated risk of bacterial infection, it is highly desirable to design coatings that are bactericidal. More recently, hydrophilic coatings using 3,4-dihydroxyphenylalanine (DOPA) and dopamine have been used to modify the surface of microporous polyethylene (PE), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE), polysulfone, etc. membranes. The strong adhesive properties of these compounds formed films that attached well to the hydrophobic membranes and decreased the contact angle from 50° to 30° . PEG-modified

polydopamine coatings showed additional resistance to protein and bacterial adhesion.

Compared with the traditional hydrophilic antifouling membrane surfaces, amphiphilic membrane surfaces engineered by the “forced surface segregation” method were demonstrated to exhibit ultralow membrane fouling. The amphiphilic surfaces bearing mixed brush architecture comprised of both hydrophilic blocks and low surface energy blocks are also suggested to be potential antifouling agents. Hydrophilic blocks generated fouling-resistant hydration layers, whereas low surface energy blocks which formed amounts of nonadhesive microdomains played a major role in repulsing the foulants away from the surfaces. Surface modification with zwitterionic molecules and polymers is believed to be the most effective method to counter all types of fouling (Tripathi et al. 2013). Zwitterionic surfaces and

membranes can be obtained by reacting different sultones with amine group containing polymers such as chitosan, polystyrene-poly-4-vinylpyridine block copolymer, etc. Incorporation of nanoparticles into polymeric filtration membranes such as silica, Al_2O_3 , and TiO_2 etc. also reported to enhance the antifouling performance of the membranes because the presence of hydrophilic nanoparticles in the polymer matrix enhances its overall hydrophilic behavior. Nano-sized TiO_2 has received significant interest for its high hydrophilicity, chemical stability, and antibacterial properties (Mansouri et al. 2010). In addition, anatase TiO_2 could serve as a photocatalyst to degrade pollutants during wastewater treatment while having an antimicrobial effect in the presence of UV.

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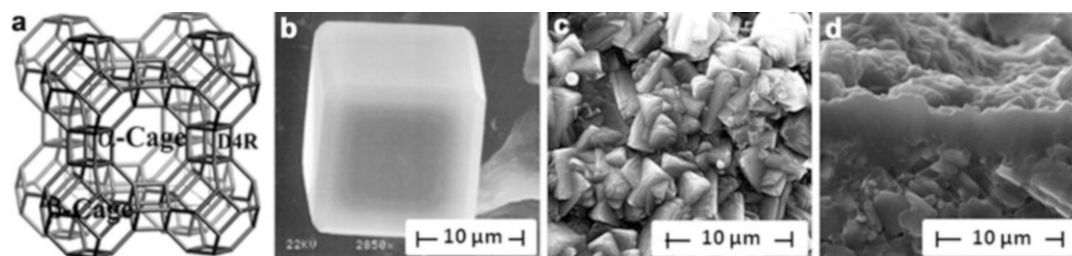
LTA Zeolite Membranes

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LTA zeolite membrane is one of the most well-studied zeolite membranes for the separation of light gases and dewatering of organics. LTA (Linde type A) zeolite has a three-dimensional pore structure, consisting of secondary building units (SBUs) 4, 6, 8, and 4-4 (Meier et al.). An example material is NaA zeolite (Linde type A sodium form) with chemical formula of $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$. The unit cell of NaA zeolite is cubic ($a = 24.61 \text{ \AA}$) with Fm-3c symmetry. The pore diameter of NaA zeolite is defined by an eight-member oxygen ring with size around $4.3 \text{ \AA}$. Generally, LTA zeolite membranes exist in the form of composite membranes, for which porous ceramic supports, typically alumina tubes, are usually used as substrates. The effective LTA zeolite separating layer is usually in the thickness of several microns (Fig. 1).

The most used strategies for the synthesis of LTA zeolite membranes are in situ synthesis and secondary (seeded) growth. Microwave techniques combining with these strategies have been applied for the synthesis of LTA zeolite membranes (Li et al. 2008). As compared with conventional hydrothermal synthesis, microwave synthesis of zeolite membranes has the



LTA Zeolite Membranes, Fig. 1 (a) Framework structure of LTA zeolite, (b) typical SEM image of a NaA zeolite single crystal, (c, d) typical SEM image of a LTA zeolite membrane

advantages of shorter synthesis time, better membrane performance, and easier to scale up.

LTA zeolite membrane has been extensively studied for the separation of light gas mixtures, e.g., H_2/CH_4 , O_2/N_2 , and $\text{n-C}_4\text{H}_{10}/\text{i-C}_4\text{H}_{10}$ gas pairs. The observed separation factors beyond the selectivities predicted from Knudsen diffusion are attributed to the so-called molecular sieving function. Another important application of LTA (particularly NaA) zeolite membranes is for removing water from various organics via pervaporation (PV) or vapor permeation (VP), thanks to its ultramicroporous channel structure and its hydrophilic nature. Nowadays, VP dewatering technology based on NaA zeolite membranes has been widely used in the industries of chemistry, bioenergy, electronics, pharmaceuticals, etc. Compared with azeotropic distillation, pressure swing adsorption (PSA), and polymeric membranes, zeolite membrane can remarkably reduce the energy consumption for dewatering of organics (Van hoof et al. 2004).

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LTA Zeolite Membranes in Pervaporation

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LTA Zeolite Membrane in Pervaporation. Pervaporation (PV) or vapor permeation (VP) is a membrane-based separation process which

LTA Zeolite Membranes in Pervaporation, Table 1 Typical PV/VP performances of LTA zeolite membrane for dewatering organics

Feed solution (10 wt.% of water)	Temperature [°C]	Water flux (kg/m ² h)	Separation factor
Water/methanol	65 (PV)	0.6	116
Water/ethanol	65 (PV)	1.0	10,000
Water/ethanol	120 (VP)	3.1	10,000
Water/n-propanol	110 (VP)	2.5	10,000
Water/i-propanol	65 (PV)	1.8	10,000
Water/ethyl acetate	65 (PV)	1.2	10,000
Water/acetone	50 (PV)	0.9	10,000
Water/i-propylamine	105 (VP)	3.2	10,000

shows a high efficiency for the separation of azeotropes and close-boiling mixtures (Huang 1991). In general, zeolites with low Si/Al ratio can be adopted to produce hydrophilic pervaporative membranes for dewatering of organics, as exemplified by LTA, FAU, SOD, and T-type zeolites (Bowen et al. 2004). Among those, LTA zeolite membranes exhibit the highest water to alcohol selectivity up to present, owing to its lowest Si/Al ratio and proper pore size (0.4 nm) that can block organic solvent molecules bulkier than water. LTA zeolite membranes have been widely used for dewatering various organics, including alcohols, aldehydes, ketones, ethers, esters, amines, and amides. Typical performances of LTA membrane are listed in Table 1.

LTA zeolite membrane is the first zeolite membrane to be used in large-scale industries for the dehydration of alcohols (Morigami et al. 2001). Nowadays, commercial LTA zeolite membranes (in NaA form) can be bought from the Japanese company, the Nano-Research Institute Inc. (XNRI), a 100 % subsidiary of Mitsui & Co., the European alliance between Smart (UK) and Inocermic, and most recently the Chinese company, HST Co. Ltd., located at Dalian.

Compared with azeotropic distillation and pressure swing adsorption (PSA), LTA zeolite membrane can remarkably reduce the energy consumption for dewatering of organics. Taking the production of anhydrous ethanol as an example, LTA zeolite membrane-based VP process can

reduce the consumption of steam by 40 % and cooling water by 30 % compared with PSA, respectively.

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Macrocapsules

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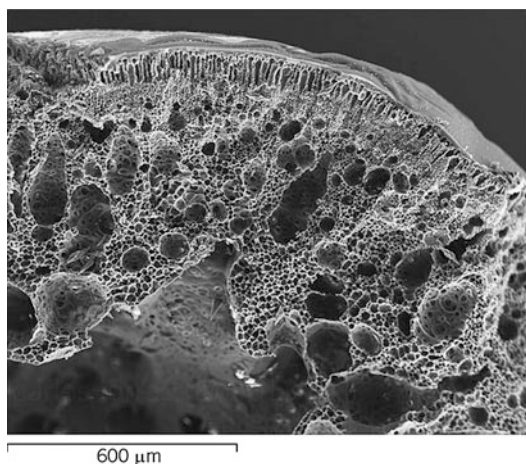
Solid material with a circular cross section (or with circularities near 1). Typical sizes of macrocapsules (also named capsules) are between hundreds of micrometers to millimeters. Macrocapsules have a thick porous wall with a small empty core (or nonexistent empty core) (Pena et al. 2009). This characteristic causes the differentiation between them and macrospheres, which are similar but have a dense and thin wall and a large empty volume inside (Lakshmi et al. 2012).

A main use of macrocapsules is to store compounds inside, which are released in a controlled way and from different parameters (Pena et al. 2009). First of all, there should be a driven force that usually is concentration gradient. Secondly, permeability occurs through the wall due to convection and diffusion. Depending on the type of process, each of them can be the predominant. For instance, considering macrocapsules with dense and thick wall, where only a concentration gradient occurs, diffusion is predominant and allows releases that can last several days (Zhang et al. 2005). On the other hand, the release process can start after an external stimulus to the

wall (i.e., light) (Bogdanowicz et al. 2013), which can cause its breaking and the immediate release of the macrocapsule contents (thus, convection being the predominant mechanism).

Often, macrocapsules are manufactured from polymer due to the simplicity of the process, capacity to control the porous structure of the wall, and cost (specially compared with inorganic materials). Immersion precipitation (a type of phase inversion) can be used to obtain macrocapsules. First, the polymer is dissolved in a solvent. Second, drops are obtained (for instance, with a needle). Finally, drops are immersed in a bath containing the non-solvent, which makes the polymer precipitate and obtain the macrocapsules (Gumi et al. 2009). Conditions of this process allow controlling the porous structure of the wall. Several variables exist: type of polymer, polymer concentration, type of solvent, type and composition of the non-solvent, bath temperature, etc. The compound to be stored is usually added when the macrocapsule is being fabricated and when the polymeric fluid is obtained.

Two main characterizations are performed with macrocapsules: release experiments and physical characterization of the macrocapsule to check their porous structure, hydrophilicity, etc. (Zhang et al. 2005). The second one is performed using the same methods as for flat sheet membranes: mercury porosimetry, scanning electron microscopy (SEM), contact angle, etc. To check the wall porous structure with SEM, the macrocapsule



Macrocapsules, Fig. 1 SEM cross section micrograph of a broken macrocapsule, showing the wall porous structure

should be broken (not cut to avoid wall damage). It can be performed using a cryotome or breaking the capsules within liquid nitrogen after swelling (i.e., ethanol) (Zhang et al. 2005; Torras et al. 2007) (Fig. 1). An option to check visually the porous structure of the macrocapsule without breaking it is by using a confocal laser scanning microscopy after swelling the macrocapsule with a proper fluorescent agent (i.e., rhodamine) (Lamprecht et al. 2000).

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Macroporous, Mesoporous, and Microporous Membranes

Lidietta Giorno, Emma Piacentini and Fabio Bazzarelli

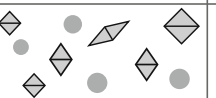
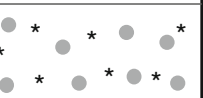
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Macroporous membranes consist of a solid matrix with defined holes or pores which have diameters larger than 50 nm (Strathmann et al. 2006). These types of membranes are used in driving force pressure process such as microfiltration (MF) and ultrafiltration (UF). They can be classified according to:

1. The type of materials: organic (polymers) and inorganic (glasses, metals, and ceramics)
2. Their structure: symmetric and asymmetric
3. Their configuration: flat sheet, hollow fiber membrane, capillary, and tubular

The separation of solutes by macroporous membranes is mainly a function of molecular size and pore size distribution. The methods are used for making membranes are phase inversion, sintering, stretching, track etching, template leaching, slip casting, and sol-gel process.

Mesoporous membranes consist of a solid matrix with defined holes or pores which have diameters in intermediate range between 2 and 50 nm (Strathmann et al. 2006).

Membrane type	macro-porous	meso-porous	micro-porous	non-porous			
Pore size (nm)	> 50	2 - 50	< 2	no permanent pores			
Separated components							
 suspended solids	 viruses	 bacteria	 colloids	 proteins	 sugars	 soluble salts	 gases/vapours

Macroporous, Mesoporous, and Microporous Membranes, Fig. 1 Schematic classification of membranes, related processes, and separated components

Mesoporous membranes are used mainly for nanofiltration (NF) process. A hydrostatic pressure is applied to transport molecule mixture mass across the membrane. They can be classified according to:

1. The type of materials: organic (polymers) and inorganic (glasses, metals, and ceramics)
2. Their structure: symmetric and asymmetric
3. Their configuration: flat sheet, hollow fiber membrane, capillary, and tubular

The methods are used for making membranes are phase inversion, sintering, stretching, track etching, template leaching, slip casting, and sol-gel process.

The separation of solutes by mesoporous membranes is a function of molecular size, pore size, distribution and electrostatic interaction.

Microporous membranes consist of a solid matrix with defined holes or pores which have diameters smaller than 2 nm (Strathmann et al. 2006). They can be classified according to:

1. The type of materials: organic (polymers) and inorganic (glasses, metals, and ceramics)
2. Their structure: symmetric and asymmetric
3. Their configuration: flat sheet, hollow fiber membrane, capillary, and tubular.

This type of membrane can be used for gas separation and dialysis.

The transport is based on diffusion model. The driving force for gas separation and dialysis is represented by pressure and concentration gradient respectively.

The methods are used for making membranes are phase inversion, sintering, stretching, track etching, template leaching, slip casting, and sol-gel process.

The schematic representation of such classification is illustrated in Fig. 1.

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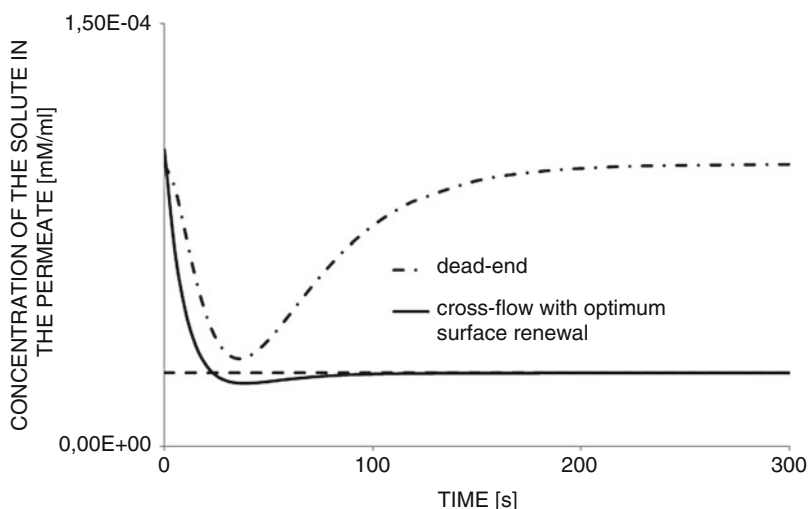
Macrosolute

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Macrosolute represents an operational term from the field of membrane filtration which denotes solute(s) of particle size(s) larger than ones that pass through a membrane (microsolute) of a

Macrosolute, Fig. 1

Comparison of cross-flow and dead-end filtration in terms of permeate concentration



specified pore size or permeability limit. Membrane filtration may be used to treat such solution (system with macrosolute, microsolutes, and solvent) to concentrate valuable macrosolute in this solution and to get rid of (or dilute) lower molecular weight impurities (Fig. 1).

Distinction of species considered as macrosolute depends on membrane process which is used to treat the solution (Cheryan 1998). In case of:

- Microfiltration – macrosolute is represented by suspended particles and bacteria bodies.
- Ultrafiltration – macrosolute presents macromolecules (typically proteins) and species with larger particle sizes
- Nanofiltration – dissociated acids and divalent salts, sugars, and species with larger particle sizes can be concentrated in solution.
- Reverse osmosis – only water passes through the membrane, and thus the term macrosolute stands for any other species present in the solution.

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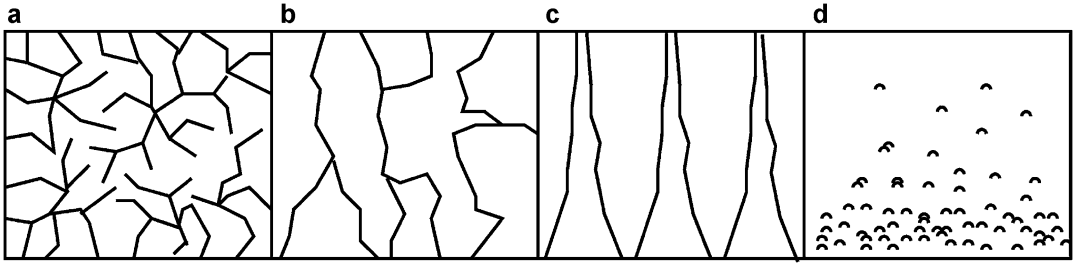
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Magnetic Membranes

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Magnetic membranes are membranes that show a measurable, nonzero, magnetic induction. Since we consider the membranes for separation, they belong only to two classes, i.e., polymeric (organic) and inorganic (ceramic) (Baker 2004; Li 2007). In both types of matrixes the magnetic powder can be dispersed, and after the membrane is formed, it is exposed to a strong magnetic field for final magnetization. Depending upon the size of the magnetic powders used as fillers, we can have: milli-, micro-, and finally nanomagnetic membranes. The process of formation is crucial in case of magnetic membranes. So far the classical casting methods have been used (Rybak et al. 2009; Dudek et al. 2012) by which the polymer solution with a magnetic powder in it is kept under the weak magnetic field to prevent the powder from sedimentation and to stimulate the formation of pores. The final structure of pores is crucial for transport properties of magnetic



Magnetic Membranes, Fig. 1 Fractal and regular clusters of magnetic particles in the magnetic membrane's cross-section

membranes. There are quite a few options here. Namely, pores can form a cluster (or a percolating cluster) of fractal or nonfractal topology, pores can form a regular inhomogeneous network that can show the $D(x)$ dependence, and, finally, the two-phase system can be obtained, i.e., metallic powder – polymer bulk in case when sedimentation is allowed (no magnetic field during casting).

These cases can be illustrated in Fig. 1.

It is interesting to notice that C and D of the regular inhomogeneous membranes can be produced by compacting magnetic powders and then magnetized in a strong magnet. A strong magnetic gradient across the membrane can be obtained in this way.

A suitable mathematical description of the separation process through such membranes follows (please, note that only one component of the mixture is sensitive to the magnetic field, like oxygen in the oxygen-nitrogen mixture):

There are two distinguished cases in the mathematical description of the above (for the mixtures of two components):

1. The system is weakly coupled, i.e., the individual components do not “see” each other being transported with almost no influence of the other. In such case the description reads (Strzelewicz and Grzywna 2007; Rybak et al. 2009):

$$\begin{aligned}\frac{\partial c_1}{\partial t} &= D_{11} \frac{\partial^2 c_1}{\partial x^2} + D_{12} \frac{\partial^2 c_2}{\partial x^2} - k \frac{\partial c}{\partial x} \\ \frac{\partial c_2}{\partial t} &= D_{22} \frac{\partial^2 c_2}{\partial x^2} + D_{21} \frac{\partial^2 c_1}{\partial x^2}\end{aligned}$$

with initial and boundary conditions

$$\begin{aligned}c_1(x, 0) &= 0 & c_1(0, t) &= c_1^0 & c_1(l, t) &= 0 \\ c_2(x, 0) &= 0 & c_2(0, t) &= c_2^0 & c_2(l, t) &= 0\end{aligned}$$

For the most favorable case $D_{12} = D_{21} \approx 0$, and D_{11} and D_{22} are constant.

When taking into account the structure and morphology (case A) of the separation membranes, we have to refine this simple description by replacing and D_{11} and D_{22} (Krasowska et al. 2012):

$$\frac{\partial c_i}{\partial t} = \frac{D_{0i}}{x^{d_f-1}} \frac{\partial}{\partial x} \left(x^{d_f-\theta-1} \frac{\partial c_i}{\partial x} \right)$$

where:

c_i – concentration of the species i

D_{0i} – diffusion coefficient of a membrane with no magnetic powder

d_f – the fractal dimension of the magnetic membrane structure which may be estimated by the box-counting method for a cross section or a face optical microscopy image of the membrane

θ – the scaling coefficient for the variance of the diffusive front $\langle x^2 \rangle \sim t^{\frac{2}{2+\theta}}$

or (case B) (Borys et al. 2011b):

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i(x, B) \frac{\partial c_i}{\partial x} \right)$$

where:

c_i – concentration of the species i

D_i – diffusion coefficient of species i , which depends upon the position (to reflect the inhomogeneous structure of magnetic particles in the membrane along its thickness)

and upon the magnetic field B (to introduce the magnetization dependent reorganization within the membrane structure and permeating particle interactions).

For case B the Knudsen diffusion equation should be used (Kruczek et al. 2006).

2. A coupled system, i.e., a system where its component transport is affected by the presence of the others. There is a few alternative ways of describing such systems (Grzywna and Stolarczyk 2005). One of the less popular but very effective is the choice of hyperbolic diffusion equation (Grzywna and Łuczka 1991; Grzywna and Stolarczyk 2005; Borys and Grzywna 2006; Borys et al. 2011a). Using this idea we can write:

$$\frac{\partial c}{\partial t} + \tau \frac{\partial^2 c}{\partial t^2} = D(x) \frac{\partial^2 c}{\partial x^2} + \frac{1}{2} D'(x) \frac{\partial c}{\partial x}$$

where τ is the correlation time during which test particle moves in a fixed direction and then after it is perturbed to choose a new direction. $D(x)$ is the diffusion coefficient.

Please note that the functional form of $D(x)$ provides modelling of both attractive forces, responsible for correlation, when $D(x)$ is an increasing function of x and repulsive forces otherwise.

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Magnetic Nanoparticles

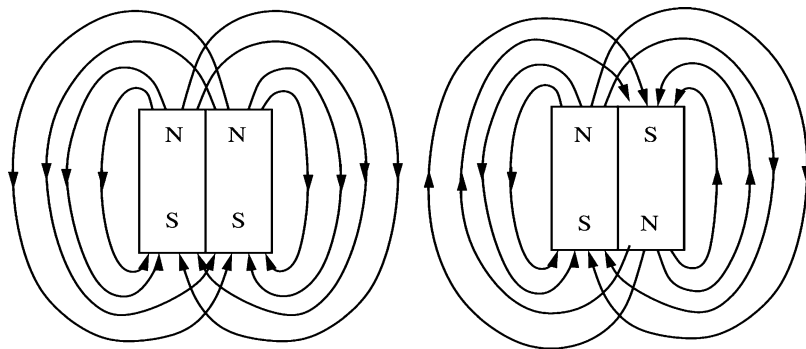
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Definition

Magnetic nanoparticles are types of nanoparticles that respond to magnetic field. According to the meaning of the term “nano,” they should fit in the range between 1 and 100 nm.

Magnetic nanoparticles are types of nanoparticles that respond to magnetic field. According to the meaning of the term “nano,” they should fit in the range between 1 and 100 nm (Gubin 2009). Such size can be sufficient to strip a magnetic material down to a single magnetic domain which may correspond, for example, to a diameter of 15 nm for Fe or 55 nm for Ni (Lu et al. 2007).

The single-domain limit follows easily from the consideration of the alignment of magnetic moments within a ferromagnetic particle (a typical example of magnetic order used in magnetic nanoparticles (Gubin 2009)). The spin-exchange interaction, which is responsible for the ferromagnetic properties of the substance, tends to align the

Magnetic Nanoparticles,**Fig. 1** Energetic state of a magnetic particle in relation to the internal magnetic moment structure

magnetic moments in a single direction (Morrish 1965; Feynman et al. 1963) which however causes an increase in the magnetic field, surrounding the magnetic particle. The energy density of magnetic field surrounding the magnet reads (Feynman et al. 1963):

$$W = \frac{B^2}{2\mu_0}$$

Looking at the Fig. 1 below, the case on the right displays a lower magnetostatic energy, because the field lines outside the material point in the opposite directions and cancel out (Morrish 1965; Feynman et al. 1963). It seems thus that the partition into two domains is desired from an energetical point of view, but the spin-exchange interaction makes the situation look more complex. The spin-exchange interaction provides a tendency to align spins in the same direction, and the formation of a domain that is oriented antiparallel to the other violates this tendency in the region of a domain wall (Morrish 1965; Feynman et al. 1963; Spaldin 2011).

The spin-exchange interaction is very strong. It was proposed by Weiss (Morrish 1965) that the magnetic energy of a dipole under the spin-exchange interaction should be sufficient to enforce order within a domain until the thermal energy exceeds it at Curie temperature (the temperature after which a ferromagnetic material behaves like a paramagnetic material) (Spaldin 2011). Taking as an example the Curie temperature equal to 1,000 K, the equivalent Weiss field acting on a single Bohr magneton could be estimated as being equal to:

$$B_W = \frac{k_B T}{\mu_B} \approx 1500 \text{ T}$$

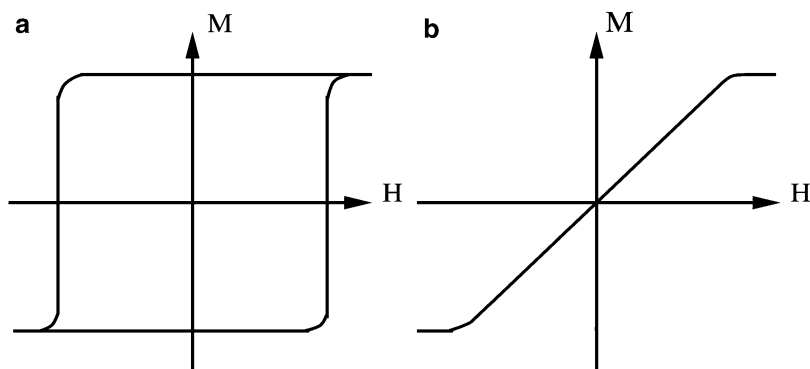
This is very large compared to the normal fields of strong magnets, which may reach 1.25 T for a FeNdB magnet (Bauer et al. 1996). However, the spin-exchange field acts only on molecules that are closely localized in space (in the atomic range).

For a very small particle, the energy lost due to the spin-exchange interaction while forming a domain with antiparallel-oriented magnetic moment is larger than the energy gain in magnetostatic energy. As the size of magnetic particles becomes larger, the magnetostatic energy grows (in proportion to the number of magnetic dipoles, so to the magnet volume, $V \sim r^3$). At some size the perturbation in the spin-exchange energy related to creation of a domain wall (which affects a thin layer of unaligned magnetic dipoles, so it is proportional to the surface $S \sim r^2$) becomes less than the gain in magnetostatic energy. At this point a domain is formed. This happens for Fe at a diameter of 15 nm and for Ni at a diameter of 55 nm for a spherical particle (Lu et al. 2007).

Except for the magnetostatic and spin-exchange energies, there are also additional energetic contributions related to magnetization like: magnetocrystalline anisotropy (there exist directions in which the magnetization is easier) and magnetostriction (changes in length of the domain due to magnetic field that create strains) (Spaldin 2011).

The single-domain magnetic particles may behave in a different manner depending on their size. For larger particles the magnetocrystalline anisotropy effects matter more (they are

Magnetic Nanoparticles,
Fig. 2 Magnetization of a
 single domain magnetic
 nanoparticle a) in the easy
 axis; b) orthogonal to the
 easy axis



proportional to the volume of magnetic particle) while for smaller particles this energy contribution drops below the level of thermal fluctuations (Lu et al. 2007; Spaldin 2011). As a consequence, the large particles can be magnetized and resemble considerable coercivity (field required to drop magnetization down to zero in a magnetized particle) and remanence (the magnetization which remains after the external field is removed). Moreover, such particles exhibit different magnetization properties in different directions (depending on whether the field direction is parallel or perpendicular to the easy axis of magnetization).

The magnetization curve for large single-domain particle is shown in the following Fig. 2:

Case (a) represents the magnetization in a direction of the easy axis. The particle is spontaneously magnetized in some direction, and to magnetize it in a reverse manner, one has to rotate the magnetization through the hard direction which requires a considerable external field (Spaldin 2011).

In case (b) the magnetization occurs in a direction that is perpendicular to the easy axis and the removal of the external field causes the magnetization to vanish by going back to the preferred easy axis (Spaldin 2011).

Finally, when the magnetic particle is small enough, the abovementioned effects cease to matter, and the particle's magnetic moment undergoes variations due to the thermal fluctuations, averaging to zero. The particle behaves then like a giant paramagnetic atom and therefore is called a superparamagnetic particle (Lu et al. 2007; Spaldin 2011). To be more specific, the review (Lu et al. 2007) provides a relaxation time formula

to reverse the magnetization in a single-domain particle. It reads:

$$\tau = \tau_0 \exp\left(\frac{E_{\text{aniz}}}{k_B T}\right)$$

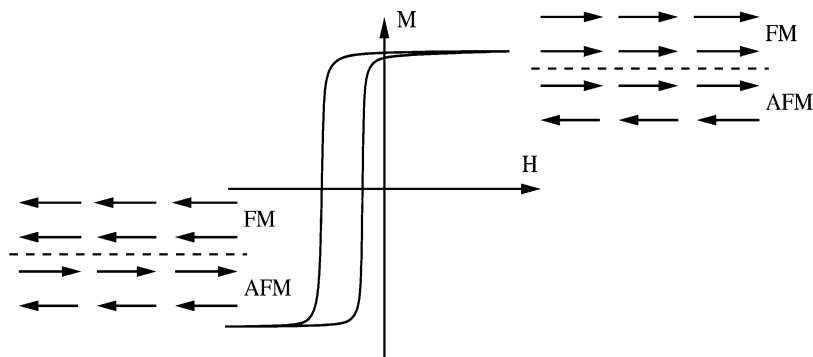
where $\tau_0 \approx 1\text{ns}$ and $E_{\text{aniz}} = K_{\text{eff}}V$ are the anisotropy energy, proportional to the particle's volume. The temperature that is on the edge of the superparamagnetic behavior is called the blocking temperature.

It is worth mentioning that the superparamagnetic particles, due to their extreme magnetic moment (which can be around $10,000 \mu_B$), allow to measure the whole magnetization curve predicted by the Langevin (or Brillouin) equation within a normal range of external magnetic fields (e.g., up to 1 T), without the need to cool the system down to extreme temperatures (Spaldin 2011).

The magnetic nanoparticles can be made from various types of materials. The most recognized is a ferromagnet (Gubin 2009), where a magnetic domain is characterized by a strict alignment of the magnetic moments (Griffiths 1999). The other is a ferrimagnet (Gubin 2009), where two subpopulations of magnetic moments exist that partially align in an antiparallel manner, canceling out part of the magnetization. This causes strong interactions between molecular spin-exchange fields of the molecules composing a ferrimagnet which, among the others, results in a complex temperature dependency of magnetization (Spaldin 2011). Finally, there are also antiferromagnetic nanoparticles (Gubin 2009; Lu et al. 2007). The antiferromagnetic materials are characterized by a

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Fig. 3 A shift in the hysteresis of a ferromagnetic nanoparticle with antiferromagnetic shell



full compensation of the magnetic moments in the bulk of the material (Spaldin 2011), which however leaves a possibility to exhibit a magnetic moment due to surface spins (Gubin 2009).

The synthesis of nanoparticles involves many approaches. The first approaches related to mechanical grinding were of limited use for metals due to their malleability (Gubin 2009). The bottom-up methods were developed, where the nanoparticles are grown from metal precursors (Gubin 2009). In such approaches one must face a problem of how to obtain a narrow size nanoparticle distribution. This relates to the problem of separation between the nucleation and growth time scales. Possible approaches in this regard involve coprecipitation, thermal decomposition of organometallic precursors (at high temperature they decompose, releasing metal which nucleates at sufficiently high concentration and then, as the growth starts and concentration drops, only growth continues), use of microemulsions, and hydrothermal synthesis (Lu et al. 2007).

The resulting particles need to be protected (e.g., from oxidation), and one needs to prevent them from agglomeration (Gubin 2009; Lu et al. 2007). This involves a coating of the nanoparticles with shells that can be surfactants and polymers (agglomeration can be prevented by electrostatic repulsive charges of the coating or by steric repulsion), inorganic components like silica, carbon, precious metals (which have low reactivity) or oxides (Lu et al. 2007).

An interesting variant of a coating is a coating of ferromagnetic nanoparticle with antiferromagnetic shell. In such case the interaction of ferromagnet and antiferromagnet (under the

spin-exchange) results in “pinning” of the magnetization to a certain direction. This causes the hysteresis loop of a ferromagnet to shift on the external field axis from the center to a side, because one of the magnetizations becomes unfavorable with respect to the alignment of the magnetic moments of an antiferromagnet (Lu et al. 2007; Spaldin 2011). The figure below that illustrates this idea is sketched after (Spaldin 2011). Observe that in the lower left corner, the alignment of the ferromagnet (FM) with respect to antiferromagnet (AFM) is not favorable (Fig. 3).

The magnetic particles have been applied to the membrane processes, for example, in works (Strzelewicz and Grzywna 2007; Rybak et al. 2009, 2012; Borys et al. 2011) devoted to the enrichment of air in (paramagnetic) oxygen, where micrometer grained particles were used, and in further projects nanoparticles were applied (Dudek et al. 2013, 2012; Strzelewicz et al. 2013; Krasowska et al. 2012). Recently the magnetic nanoparticles were applied in the artificial gill project (Velianti et al. 2014).

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Magnetically Responsive Membranes

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Synonyms

Environmentally responsive membranes; Multifunctional responsive membranes; Responsive membranes; Smart membranes; Stimuli-responsive membranes

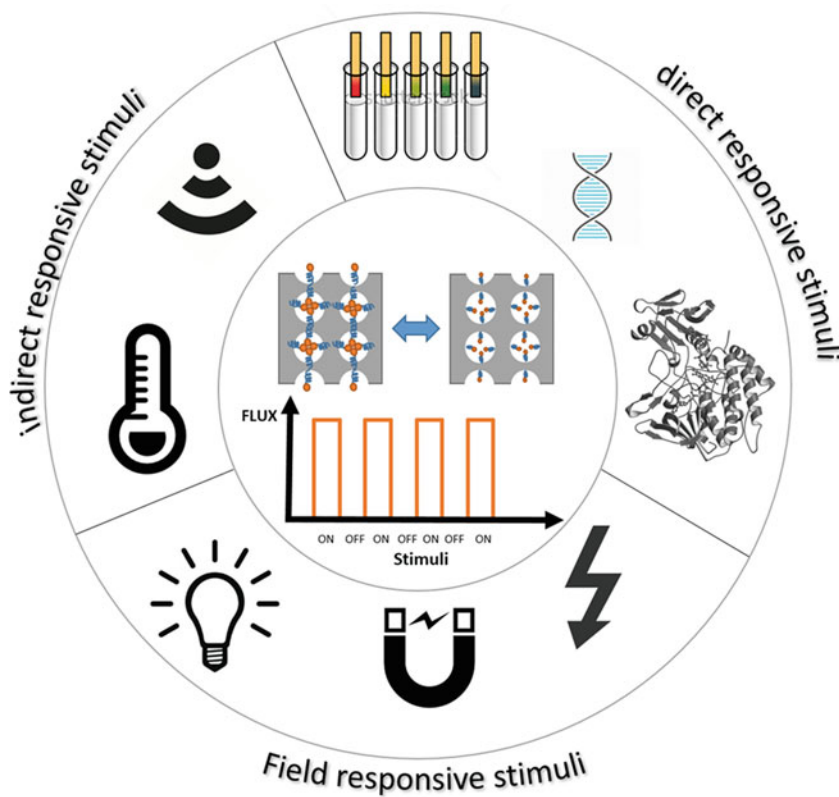
Introduction

Responsive membranes represent a new class of advanced membranes that respond to an external stimulus (Bhattacharyya et al. 2012; Wandera et al. 2010). They are a subset of multifunctional membranes where the membrane performs more than one function simultaneously. The development of responsive membranes has been inspired by biological membranes such as skin and epithelial tissue. The barrier properties of biological membranes can be modulated by environmental conditions such as temperature, humidity, presence of a specific ion, etc. Responsive membranes mimic this behavior allowing for modulation of membrane performance by environmental conditions. In general, in the case of porous membranes, responsive behavior is imparted by grafting responsive polymer layers onto the membrane surface. For nonporous membranes the responsive groups are often part of the membrane polymer (Husson 2012).

Stimuli-responsive membranes make use of the interplay between membrane structure and changes in polymer conformation, polarity, and reactivity (Darvishmanesh et al. 2015). Responsive behavior occurs in two steps: an environmental trigger causes a conformational and/or property transition at the microscopic level which is then amplified to a macroscopically measurable change in membrane performance. Responsive behavior is a result of changes in polymer chain conformation and/or property. Changes in polymer chain conformation and property are due to variations in protonation or deprotonation, hydrophilicity/hydrophobicity, charge density and distribution, solvation free energy, etc. The conformational change is driven thermodynamically to minimize the Gibbs free energy of the polymer/solvent system (Du et al. 2010).

Types of Stimuli

Responsive behavior may be categorized according to the type of stimulus used to elicit polymer conformational and/or property changes



M

Magnetically Responsive Membranes, Fig. 1 Types of stimuli (Reprinted from *Current Opinion in Chemical Engineering*, vol number: 8, Siavash Darvishmanesh,

Xianghong Qian, S Ranil Wickramasinghe, *Responsive membranes for advanced separations*, 98–104, 2015, with permission from Elsevier)

(Darvishmanesh et al. 2015). Figure 1 (Darvishmanesh et al. 2015) gives a schematic representation of the three types of stimuli: direct, indirect, and field induced. Direct stimulation is specific. The responsive groups on the membrane respond to a specific chemical or biological cue. For example, pH-responsive groups respond to changes in pH (H^+ ion concentration) (Himstedt et al. 2013a; Gugliuzza 2013; Wee et al. 2013). A carboxylic group (e.g., acrylic acid) at pH below its pK_a is protonated leading to its decreased hydration and de-swelling effect. The polymer network swells when the pH exceeds its pK_a as the carboxylic groups become deprotonated and repel each other. Thus membrane permeability can be adjusted. In the case of pH-responsive groups, a number of different weak base and acid groups respond to a specific chemical cue, H^+ ions in solution.

Solution ionic strength is another example of a direct stimulus and can affect the degree of polymer swelling in a number of ways. The presence of salt ion and its type and concentration affect charge interactions in the membrane/solution system. It affects the degree of swelling for pH-responsive membranes. Salt ions can cause charge screening thus limiting the amount of swelling. Strong acid and base groups such as quaternary amines are insensitive to solution pH but respond to changes in ionic strength (Husson 2012). In addition poly (zwitterion)-based multilayer membranes have also been shown to respond to solution ionic strength (de Grooth et al. 2014). However unlike weak polyelectrolytes such as weak acids and weak bases, increasing ionic strength leads to an increase in swelling.

Biologically inspired responsive groups include (i) antigen-responsive membranes

(Zhang et al. 2007; Lu et al. 2003), (ii) redox/thiol-responsive groups (Wong et al. 2008; Cerritelli et al. 2007; Ghosh et al. 2009), (iii) enzyme-responsive membranes (Ulijn 2006), and (iv) glucose-responsive membranes (Chu et al. 2004). In these cases a chemical or biological cue directly interacts with a specific chemical groups on the membrane surface. Thus they are much more specific than the pH and ionic strength-responsive group describe above.

Indirect stimulation, like direct stimulation, involves mass transfer to the responsive groups. However unlike direct stimulation, changes in polymer conformation/property occur due to changes in the thermodynamic environment and not to a specific interaction with a chemical or biological cue. Most temperature-responsive polymers display a lower critical solution temperature (LCST). A common example is poly (N-isopropylacrylamide) (PNIPAM). PNIPAM is a hydrogel that is water soluble when the temperature is below its LCST. Above its LCST, the polymer becomes hydrophobic and will phase separate. When PNIPAM chains are attached to a membrane surface, the grafted polymer layers swell and de-swell when the local temperature fluctuates below or above the LCST. Previous studies have shown that conformational switching can lead to the release of adsorbed foulants (Wandera et al. 2011, 2012; Tomer et al. 2009). The LCST of thermo-responsive polymers is strongly affected by the salt ion, its type, and concentration. An increase in concentration will lead to a decrease in LCST. The actual decrease in ionic strength depends on the specific ion present in solution. Recent studies suggest that modulation of LCST by solution ionic strength could be used to develop high-performance ligands for applications such as membrane-based hydrophobic interaction chromatography (Wu et al. 2014; Himstedt et al. 2013b).

Ultrasound represents another method of indirect stimulation. Ultrasound-responsive membranes have been reported for biomedical applications such as controlled drug release. To date most responses to ultrasound waves lead to irreversible cleavage of weak bonds in the polymer structure. Consequently, unlike the

other responsive mechanisms described here, ultrasound-responsive membranes tend to undergo irreversible transformations (Li et al. 2010; Zhang et al. 2009). Development of reversible ultrasound-responsive polymers that undergo reversible transformations could be an area of future development.

Field-induced responsive behavior is fundamentally different to the direct and indirect responses as no mass transfer is required. Three types of external field, electric, magnetic, and electromagnetic waves, have been considered in the past. Electric field-responsive membranes shrink, swell, or twist in response to an external electric field due to the interaction of charged species with the external field. These changes in polymer confirmation can be used to control solute permeation through the membranes. In addition development of fouling-resistant membranes based on desorption of adsorbed solutes due to changes in polymer conformation induced by changes in an external electric field has been described (Wandera et al. 2010).

Magnetic field-responsive groups such as magnetic nanoparticles are usually physically entrapped within the membrane structure or immobilized onto the membrane surface. Changes in an external magnetic field can cause movement and/or heating of these magnetically responsive groups. Recent studies indicate that movement of magnetically responsive polymer chains attached to the membrane surface can suppress concentration polarization during nanofiltration (Himstedt et al. 2011; Yang et al. 2013). In addition magnetically responsive polymer chains attached to the inside pore surface of microfiltration membranes can be used to modulate membrane permeability by applying an external magnetic field (Himstedt et al. 2012).

Electromagnetic radiation such as UV, IR, etc. has been used to trigger structural transformations of functional species such as azo groups (Ishihara et al. 1984; Ishihara and Shinohara 1984; Kinoshita et al. 1986). For example, photo-responsive polyethersulfone (PES) membranes were prepared from blending PES with azobenzene(Azo) and β -cyclodextrin(β -CD). The water permeability of the membranes was

tested under light irradiation at 450 and 365 nm, respectively. At 450 nm, the membrane pores close and water flux decreases due to the complex formation between Azo and β -CD. By changing irradiation wavelength to 365 nm, the membrane pores open due to complex dissociation between Azo and β -CD, and the membranes show higher permeability.

Outlook

Though very much in its infancy, development of responsive membranes offers numerous opportunities for designing high-performance membranes for future separations needs. It is likely that more complicated responsive mechanisms that involve a cascade of stimuli-response interactions will be developed analogous to biological membranes. It is also likely that computational simulations will provide valuable guidance when developing the appropriate nanostructures for these advanced membranes.

Cross-References

► Polymeric Magnetic Membranes

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Maleic Anhydride Production by Membrane Reactor

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Maleic anhydride is a valuable intermediate product in the manufacture of polyester fiber, succinic acid, tetrahydrofuran, tartaric acid, and several other chemicals. Most of the maleic anhydride is produced by the oxidation of butane with VPO catalyst. This reaction is unique because no other commercial process achieves the insertion of three oxygen atoms in one paraffin molecule in a single step using molecular oxygen. The catalyst is a complex mixture of vanadium and phosphorous oxides, which is often close to the chemical composition of vanadyl pyrophosphate, but in fact the oxidation degree of vanadium varies between +4 and +5 depending on the operating conditions.

Industrial operation is limited by need to avoid explosive atmospheres, which requires low butane or low oxygen concentration. In conventional reactors a low oxygen concentration would imply a too low butane conversion, which would be economically unsuitable. Therefore the industrially employed approach, both for fixed and fluidized bed reactors, is to feed a low butane concentration (typically below 2 %) in air. This approach implies the use of large feed and product flows, increasing the operating and capital costs. The use of a membrane reactor allows the operation with a large butane concentration (up to 10 % butane) but avoiding the coexistence in a given point of large butane and oxygen concentrations (Mallada et al. 2000), in a similar way as when membrane reactors are used for oxidative dehydrogenation. A critical point in this kind of reactor is to avoid too low oxygen concentrations, since a reducing atmosphere changes the oxidation degree of vanadium, with a catastrophic decrease in selectivity.

A way to decrease the risk of vanadium reduction is using CO₂ as inert gas. In fact, there are experimental proofs that under reaction conditions, CO₂ is not fully “inert” but can contribute to achieve a more oxidized catalyst (Mallada et al. 2002; Xue et al. 2001).

Another factor that may contribute to improve the maleic anhydride yield in a membrane reactor is the catalyst bed configuration. If the catalyst bed is located around the membrane, instead of inside, the achievable yield increases. A mathematical model of both reactors explains this result by the differences in radial partial pressure profiles (Pedernera et al. 2000).

Finally, in order to apply a membrane reactor industrially, the temperature control is critical. While fixed bed reactors use a bath of fused salts to keep the catalyst bed temperature under control, this approach would not be feasible in membrane reactors. A method proposed to control the temperature in a membrane reactor is to surround the reactor with a fluidized bed. The high isothermicity and excellent heat exchange are well-known characteristics of fluidized beds, and the same oxygen containing stream that is permeated through the membrane can be used to keep

the bed fluidized. This configuration has been employed in a pilot plant (Alonso et al. 2001).

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Manganese Removal by Liquid Membranes

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Manganese is the chemical element having the symbol Mn and atomic number 25. It is an essential trace nutrient in all forms of life: it serves as a necessary constituent of metalloproteins including enzymes since it optimizes enzyme and membrane transport function. Although the toxicity of manganese compounds is lower than those of other widespread metals, such as nickel and copper, both its excess and deficiency in the body can cause serious impairment of vital physiological and biochemical processes. Excessive manganese intake is most frequently associated with the so-called manganism, a rare central nervous system disorder, characterized by symptoms similar

to Parkinson's disease (weakness, monotone and slowed speech, tremor, disorientation, memory impairment, anxiety, and hallucinations).

Manganese compounds, in which it has various oxidation states, are widely used in the industry. Manganese dioxide is used in dry cell batteries as a depolarizer and in glassmaking as a drying agent. Depending on their oxidation state, manganese ions have various colors and are used industrially as pigments. The permanganates of alkali and alkaline earth metals are powerful oxidizers, so that they are used as a bactericide and algicide in water treatment and as an oxidant in organic chemical synthesis. Since manganese is used in these and other different industrial processes, its separation and/or recovery from the various liquid effluents or wastewater is of practical value.

A variety of separation processes for metal ions have been developed for industrial needs, including precipitation, inorganic and polymeric adsorption, evaporation, and reverse osmosis. Such techniques produce water within international health standards but entail some drawbacks.

Solvent extraction procedures have proven to be very useful in the separation and/or recovery of metal ions from aqueous media, but they involve high capital and operating costs due to large inventory of solvent, especially in the case of dilute solutions. Thus liquid membrane has been proven to be a very powerful technology.

A liquid membrane (LM) is a layer of an organic phase (the so-called LM phase) that separates two aqueous solutions. An extractant (carrier), promoting the so-called facilitated transport from the donor phase (feed) to the acceptor phase (strip), may be dissolved in the organic phase (Molinari et al. 2009a, b). LM-based processes offer a technology with a lot of advantages over conventional separation techniques. The main advantages are (i) combination of extraction and stripping processes in a single stage, resulting in a low solvent consumption; (ii) uphill transport against concentration gradient; and (iii) small amounts of extractant needed, resulting in the possibility to use very selective carriers, which sometimes are not very cheap.

A widely used important acidic extractant in hydrometallurgy in metal separation and/or

recovery is di(2-ethylhexyl)phosphoric acid (D2EHPA). It is extensively used also in the extraction and recovery of manganese from neutral and weakly acidic solutions using supported liquid membrane and emulsion liquid membrane (Mohapatra and Kanungo 1992). Some studies (Yongtao et al. 1992) considered the simultaneous extraction and concentration of cadmium and manganese from aqueous solutions obtaining recoveries of cadmium and manganese in the range of 92–100 %. Recently a novel method for Mn(II) extraction from sulfuric acid solutions has been proposed (Sadyrbaeva 2011) which involves electrodialysis and a bulk liquid membrane containing D2EHPA as the carrier. To accelerate the ion transfer through the liquid ion-exchange membrane, an electric field was applied. Operating in this way, the electrodialytic process (unselective) was coupled with the liquid membrane-based process, which provides greater selectivity and permeability with respect to the traditional solid ion-exchange membrane. Complete removal of Mn(II) from a feed solution containing 0.01 mol/L of MnSO_4 and a maximum extraction degree of 88 % was obtained under optimized conditions.

Liquid Membrane as Pre-concentration Technique

Manganese could be accumulated in tissues and body fluids, like blood serum and urine. Considering the very low concentration of trace elements (manganese in our case) in these fluids, a pre-concentration step before analysis is required. According to results from a recent study (Soko et al. 2003), the D2EHPA-based supported liquid membrane technique can be used to extract and pre-concentrate Mn(II) from water, milk, and blood serum.

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Mass Intensity

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Membrane operations are well known for their modularity, compactness, and flexibility; therefore, they can be considered as new operations developed in the logic of process intensification. Recently, new metrics for comparing membrane performance with those of conventional units have been introduced (Curzon et al. 2001; Brunetti et al. 2011, 2014). These new metrics take into account the size, the weight, the flexibility, the yield, and the modularity of the plants. They are useful for having an immediate indication of the eventual gain that a membrane operation can offer with respect to a traditional one. In this sense, they are useful also for selecting the proper separation technology for a specific process.

Among them, mass intensity is a measure of the exploitation of the raw material with respect to final production or recovery of the desired product, and it can be intended as a measure of the efficiency of the process.

In order to compare different systems, it can have different definitions: it can be calculated taking into account the product and its fraction recovered (Eq. 1) as valuable product with respect to the total mass fed. It can also be calculated as the ratio between the amount of product and its fraction recovered with respect to the steam and cooling water necessary to carry out the process (Eq. 2). In the ideal situation, the mass intensity would approach 1 which means that all the inlet mass has been converted or recovered as valuable product.

$$\text{Mass Intensity}_1 = \frac{\text{Total inlet mass}}{\text{Mass of desired product recovered}} \quad (1)$$

$$\text{Mass Intensity}_2 = \frac{\text{Steam and cooling water required}}{\text{Mass of desired product recovered}} \quad (2)$$

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Mass of Immobilized Enzyme

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Enzymes can be immobilized on the membrane surface or within the membrane structure by various techniques, including physical entrapment, chemical adsorption, and chemical attachment.

Regardless of the immobilization mechanism, the methodology in general includes the use of an initial enzyme solution (or feed), of known proteic enzyme concentration and volume, that is fed to the membrane or in which the membrane is immersed. After a certain time, the solution is collected (final solution or retentate), the volume is accurately measured, and washing solutions are used to remove the enzyme present in the system that is not immobilized in a stable way.

The amount of immobilized enzyme can be determined by the mass balance between mass present in the initial, final, and washing solutions:

$$\text{mass}_{\text{enz. imm}} = \text{Mass}_{\text{initial}} - \text{Mass}_{\text{final}} - \text{Mass}_{\text{washing}}$$

The enzyme mass in each solution can be determined by the enzyme concentration and volume of the solution (mass = concentration * volume). The enzyme concentration can be measured by a protein assay method (such as biuret reaction, Lowry method, Bradford assay, bicinchoninic acid (BCA) assay (Sapan et al. 1999)). These methods rely on the denaturation and hydrolysis of the protein in corresponding amino acids followed by the reaction of amino acids (in general those bearing more reactive functional groups) with reagents that form complexes that absorb at specific wavelength in the visible spectrum.

A calibration curve prepared with protein standard solution permits to determine the concentration of the unknown sample. The use of the same type of immobilized protein as standard (if available in pure form) or pure proteins with similar amino acid content as the one used for the immobilization is necessary to have true protein estimation and accurate mass balance. In general, BSA (bovine serum albumin) is used as a protein standard.

The direct measurement of protein absorbance in the UV range (usually at 280 nm) is sometimes reported. However, it is not accurate enough since protein denaturation strongly affects the absorbance intensity, and there are evidence that when a protein is recycled along a circuit or pressed through a pore, the conformation may open (even though this might be to an extent that does not deactivate the enzyme).

The BCA assay can be used for the direct determination of covalently bound or adsorbed proteins on membranes. In the BCA assay, the colored complex that develops is a result of a secondary reaction not involving the protein itself. The principle of the assay relies on the formation of a Cu^{2+} amino acid complex under alkaline conditions, followed by reduction of the Cu^{2+} to Cu^{1+} forming a purple-blue complex that is stable and water soluble. Since the purple complex is water soluble, the color is formed and released into the supernatant instead of remaining associated with the membrane.

The membrane with the immobilized protein can be directly immersed on the reaction reagent. After the required incubation time, the membrane can be removed and the absorbance of the supernatant is read at 562 nm. The immobilized protein amount is directly determined by comparison to a standard curve obtained in the same way by using the soluble protein (or the protein standard).

The direct BCA method is therefore well suited for determining membrane-bound protein with enhanced sensitivity. It is fast and less subject to errors inherently encountered during the combination of loading and wash buffers required to do the mass balance method. This is a destructive method and therefore specific membrane samples have to be dedicated to the analyses. The amount of immobilized enzyme on the sample of membrane used for reaction rate or catalytic activity analyses is assumed similar to the one detected as it is carried out in parallel in the same conditions.

However, when selecting a method, it must be taken into account that some substances (such as buffering salts and chelators) and the membrane itself may interfere with the protein assay.

For kinetic studies of immobilized enzyme, where the accuracy of the amount of enzyme is extremely important, a cross-check with both methodologies is advised.

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Mass Transfer in Gas Separation

► [Principle of Gas Separation](#)

Mass Transfer in Microfiltration

► [Principle of Microfiltration](#)

Mass Transfer in NF

► [Principle of Nanofiltration \(NF\)](#)

Mass Transfer in PV

► [Principle of Pervaporation](#)

Mass Transfer in Reverse Osmosis RO

► [Principle of Reverse Osmosis \(RO\)](#)

Mass Transfer Resistance

► [Mass Transport Equations](#)

Mass Transport Equations

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Synonyms

[Mass transfer resistance](#)

Mass transfer is a phenomenon, generated by a concentration difference, by which a component

is transferred from a point to another. The introduction of a mass transfer coefficient is a simple way to quantify this phenomenon. Mass transfer coefficient is defined as the ratio between the component flux and the driving force generating the flux (Cussler 1997),

$$k = \frac{\text{rate of component flux}}{\text{driving force}} \quad (1)$$

The unit of the mass transfer coefficient depends on the units used to quantify flux and driving force. For example, if we express fluxes in kmol/m²s and driving force is a concentration difference (kmol/m³) then *k* will have the unit of m/s. However, reader should be aware that different units are sometime used, depending on the circumstances: fluxes can be expressed in mass rather than moles, and driving force can be a partial pressure or a molar fraction difference.

The definition of a mass transfer coefficient could not be simpler but nothing can be said a priori about its numerical value. For the way it has been defined, mass transfer coefficient is a function of the two points considered for the mass transfer, although in the vast majority of cases one point is the fluid phase (gas or liquid) bulk and the other is a system boundary, such as a tube wall or an interface. The coefficient numerical value depends on the specific system considered (flow in pipes, fixed bed of particles, falling liquid film) and on the physical parameters (such as diffusivity, density, viscosity, etc.). As it is most useful for situations where an analytical approach is not practical or too complex, its quantification relies on experimental measurements. Much effort has been devoted to generalize as much as possible data collected from experimental measurements, and this has been done by correlating the data through dimensional parameter, generally involving a suitably defined Sherwood number, containing the mass transfer coefficient, Reynolds number, and Schmidt number, in analogy with observation on heat transfer which correlate Nusselt number with Reynolds and Prandtl numbers. Practical relevant examples are the case of mass transfer taking place for the flow inside a pipe between the phase bulk and the tube wall

$$Nu = 0.026 Re^{0.8} Sc^{0.33}$$

or the flow outside and perpendicular to a capillary bed

$$Nu = 0.80 Re^{0.47} Sc^{0.33}$$

The concept of mass transfer coefficient can also be utilized when transfer between different phases is considered, such as mass transfer between a gas and a liquid phase or mass transfer between fluids separated by a dense membrane.

The definition given in Eq. 1 is still applicable although care must be taken when the driving force is to be quantified. As a descriptive example, let's consider the case of mass transfer of a component *A* taking place between the bulk of gas phase, with *p_A* the component partial pressure and the bulk of a liquid phase, with *C_A* the component concentration. The overall mass transfer coefficient can be defined in this case as the ratio between component A mass flux and overall driving force, a parameter which is given by the "homogenized" difference between *p_A* and *C_A* obtained by substituting the concentration in one phase with the corresponding equilibrium value in the other phase. In other words

$$\text{Driving force} = p_A - HC_A = \frac{p_A}{H} - C_A$$

where *H* is the parameter expressing the partition equilibrium of the component *A* between the gas and the liquid phase (which assumes a constant value if a Henry law type equilibrium applies).

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Mass Transport in Dialysis

► [Principle of Dialysis](#)

Mass Transport in Electrodialysis

► Principle of Electrodialysis

Mass Transport in Ultrafiltration

► Principle of Ultrafiltration (UF)

Materials and Structures of Synthetic Membranes

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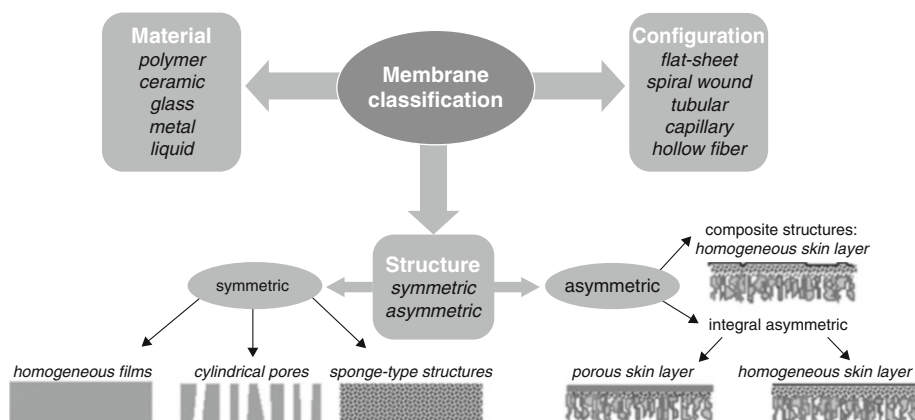
Synthetic membranes show a large variety in their physical structure and the materials they

are made from. Based on their structure they can be classified in four groups:

- Porous membranes
- Homogeneous dense solid membranes
- Solid membranes carrying electrical charges
- Liquid or solid films containing selective carriers

Furthermore, the structure of membranes may be symmetric, i.e., the structure is identical over the entire cross section of the membrane, or it may be asymmetric, i.e., the structure varies over the cross section of the membrane.

The materials used for the preparation of membranes can be polymers, ceramics, glass, metals, or liquids. The materials may be neutral or carry electrical charges, i.e., fixed ions. The membrane conformation can be flat, tubular, or a hollow fiber. The schematic drawing of Fig. 1 illustrates the morphology, materials, and configuration of some technically relevant synthetic membranes.



Materials and Structures of Synthetic Membranes, Fig. 1 Schematic drawing illustrating the various materials, structures, and configuration of technically relevant synthetic membranes (Strathmann et al. 2010)

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Mathematical Description of Mass Transport in Membranes

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Mass transport between two phases through a membrane may be the result of diffusion, convection, or migration depending on the driving forces and the structure of the membrane.

A mass transport process is referred to as *diffusion* when individual components permeate a matrix independent of each other by random movement under the driving force of a chemical potential gradient. The permeation rate in a

diffusion process depends on the magnitude of the driving force, i.e., the chemical potential gradient of the diffusing component and on its diffusion coefficient which is determined by friction between the diffusing component and other components in a mixture.

A mass transport process is referred to as *convection* when bulk flow occurs under the driving force of a hydrostatic pressure difference relative to a matrix which acts as a frame of reference. The flow velocity depends on the hydrostatic pressure difference and hydrodynamic permeability of the matrix which is determined by the friction between the solution and the matrix.

A mass transport is referred to as *migration* when charged components move through a matrix under the driving force of an electrical potential difference. The migration rate depends on the electrical potential gradient and the mobility of the components in the matrix. The mobility of a component is directly related to its diffusion coefficient and is determined by the friction between the migrating component and other components in a mixture.

In membrane processes all three forms of mass transport can contribute to the overall flux. Generally, however, one transport form is dominant while the others contribute to a lesser extent to the overall mass flux. In micro- and ultrafiltration, convection of a bulk solution is the dominant form of transport while diffusion is generally insignificant. In reverse osmosis matter is transported through the membrane mainly by diffusion of individual molecules through a more or less homogeneous membrane matrix, but convection can become significant with high-flux membranes. In electrodialysis migration of ions in an electric field is the dominant form of transport, but under certain process conditions diffusion and convection can also become relevant.

The mass transport through membranes can be described by various mathematical relations. Most of them are semi-empirical, postulating membrane models, such as Fick's law, Hagen-Poiseuille's law, and Ohm's law. A more

comprehensive description, which is independent of the membrane structure and thus of any membrane model, is based on a general phenomenological equation which connects the fluxes of electrical charges and individual components with the driving forces by a linear relation (Onsager 1931):

$$J_i = \sum_k L_{ik} X_k \quad (1)$$

Here J is a flux per unit area and generalized X is a driving force, the subscripts i and k refer to individual components and electrical charges, and L is a phenomenological coefficient relating the fluxes to the driving forces.

For multicomponent systems with fluxes of individual components and electrical charges, Eq. 1 can be written as a matrix in which the diagonal coefficients relate the fluxes to the directly corresponding driving forces and the cross coefficients express the coupling of fluxes with nonconjugated driving forces:

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + \cdots + L_{1n}X_n \\ J_2 &= L_{21}X_1 + L_{22}X_2 + \cdots + L_{2n}X_n \\ &\vdots \\ J_n &= L_{n1}X_1 + L_{n2}X_2 + \cdots + L_{nn}X_n \end{aligned} \quad (2)$$

Thus, Eq. 2 describes the mass transport through a membrane not only as a linear function of the corresponding driving forces as does, e.g., Fick's or Ohm's law, but it considers also a possible kinetic coupling between different fluxes.

In membrane processes fluxes are the result of spontaneous, i.e., irreversible, processes with a positive entropy production. The relation between the entropy production and the mass transport is given by

$$T \frac{dS}{dt} = \Psi = \sum_k J_i X_k = \sum_i \sum_k L_{ik} X_i X_k \geq 0 \quad (3)$$

Here Ψ is the dissipation function, X is a driving force, the subscripts i and k refer to individual components and electrical charges, and L is a

phenomenological coefficient relating the fluxes to the driving forces.

By introducing Eq. 3 into Eq. 2, it can be shown (Katchalsky and Curran 1965) that the diagonal coefficients are always positive, while the cross coefficients may be positive or negative. For a two-component system which has two driving forces and four phenomenological coefficients, the dissipation function is given by

$$\Psi = (L_{11}X_1 + L_{12}X_2)X_1 + (L_{21}X_1 + L_{22}X_2)X_2 \geq 0 \quad (4)$$

Since the entropy production for all positive and negative values of X_1 and X_2 must be positive, the phenomenological coefficients must satisfy the following relation:

$$L_{11} \geq 0 \text{ and } L_{22} \geq 0 \quad (5)$$

and

$$L_{11}L_{22} - L_{12}L_{21} \geq 0 \quad (6)$$

Thus, the diagonal coefficients must always be positive while the cross coefficient may be positive or negative to satisfy Eq. 4.

The number of the cross coefficients, however, is reduced by the Onsager relation (Onsager 1931) which is given by

$$L_{ik} = L_{ki} \quad (7)$$

Through the coupling of fluxes, it becomes obvious that a transport of components may be obtained without a directly related driving force. The magnitude of the fluxes obtained through a coupling with other fluxes depends on the coupling coefficient. In many cases the coupling between fluxes can be neglected. In some cases, however, it can be significant. For instance, the coupling of water with an ion flux can lead to a significant water transport through a membrane.

Equation 1 provides a very complete description of transport processes through a membrane. The only other boundary condition relevant for a system which contains charge components is that electroneutrality is required at all times on a

macroscopic scale. All phenomena observed in membrane systems, such as osmosis and electro-osmosis, the diffusion of individual components, viscous flow of the bulk solution, the electric current, the buildup of an osmotic pressure, the streaming, and the diffusion potential, as well as the different technically relevant membrane processes, can in principle be described by applying Eq. 1. For most practical applications, however, this equation is rather complex. First of all, it is only applicable close to equilibrium because of the assumed linear relationships between fluxes and driving forces. Furthermore, the many different coefficients are difficult to determine by independent measurements. The treatment becomes even more complicated if the membrane consists of a heterogeneous medium such as a micro- and ultrafiltration membrane where viscous flow is the dominant means of mass transfer in the pores when a hydrostatic pressure is applied as a driving force, but diffusion and migration can exist both in the pore medium and the solid membrane matrix.

However, in many practical applications, kinetic coupling between fluxes can be neglected and Eq. 1 can be reduced to more simple relations, such as Ohm's or Fick's law, and the phenomenological coefficients can be expressed by the electrical resistance or the diffusion coefficient.

Another approach to describe the mass transport in membrane processes is based on a relation developed by Maxwell and Stefan around 1870 and which was extended by Spiegler (1956). In this relation the forces are expressed as a linear function of the fluxes:

$$X_i = \sum_k R_{ik} J_k \quad (8)$$

Here X is a driving force, J is a flux, and R is a phenomenological coefficient relating driving forces and fluxes.

The coefficient R has the dimension of a generalized resistance and is expressed by a unit force divided by a flux. It is related to the coefficient L of Eq. 1 which has the dimension of a generalized conductance and is expressed as flux per unit force by

$$L_{ik} = \left(\frac{J_i}{X_k} \right)_{X_i} \text{ and } R_{ik} = \left(\frac{X_i}{J_k} \right)_{J_i} \quad (9)$$

The Maxwell-Stefan approach is based on the assumption that in a steady state flux, the driving forces acting on a component i are equal to the sum of the friction forces between i and other components in the system.

The flux of a component in a mixture is always expressed relative to another component, which is used as a frame of reference. Thus, the flux J_i of a component i in a mixture relative to a component k is

$$J_i = C_i(u_i - u_k) \quad (10)$$

Here u is the linear velocity of the component and C the concentration.

The flux of an individual component is always proportional to its linear velocity relative to the velocity of another component, which is used as a frame of reference. Thus, the number of independent fluxes in a given system is equal to the total number of components in the system minus the one used as reference. A system containing a membrane with n components, including the membrane, has $n-1$ independent fluxes. In membrane processes generally the fluxes through the membrane are of interest. Therefore, the membrane is used as frame of reference and its velocity is assumed to be zero.

If viscous flow is excluded, the Maxwell-Stefan equation (Wesselingh and Krishna 1990) is given by

$$\begin{aligned} X_i &= \sum_k C_i f_{ik} (u_i - u_k) \\ &= \sum_k C_i \frac{RT}{\mathcal{D}_{ik}} (u_i - u_k) \end{aligned} \quad (11)$$

or

$$J_i = \frac{\mathcal{D}_{ik}}{RT} X_i \quad (12)$$

Here X is the driving force, C is the concentration, u is the linear velocity, f is the friction coefficient, and $\mathcal{D}$ is the Maxwell-Stefan

diffusion coefficient. The subscripts i and k refer to individual components.

Combination of Eqs. 11, 12, and 1 provides the relation between the various terms of the phenomenological equations and the Maxwell-Stefan equations:

$$\sum_i L_{ik} = \frac{1}{\sum_i R_{ik}} = \frac{1}{\sum_i f_{ik}} = \sum_i C_i \frac{D_{ik}}{RT} \quad (13)$$

Equations 11 and 12 provide the same complete description of transport processes through a membrane separating two homogeneous mixtures as does the phenomenological Eq. 1. The only other boundary condition relevant for a system which contains charge components is that electroneutrality has to be fulfilled at all times on a macroscopic scale.

Mass transport in membrane processes can be achieved by applying different driving forces, such as pressure, concentration, or electrical potential gradients to a feed mixture. The different driving forces result in different membrane processes in which also different membrane structures are utilized. In micro- and ultrafiltration, for example, porous membranes are applied that separate the various components of a mixture according to their size. The transport is mainly based on convection and the driving force is a hydrostatic pressure gradient. In reverse osmosis, gas separation and pervaporation dense films are used as selective barrier for the transport of low molecular weight components. The driving force is a hydrostatic or partial pressure difference between a feed mixture and a permeate. The transport is based on diffusion. In dialysis a concentration difference is used to achieve the desired mass transport which is also based on diffusion. In electrodialysis an electrical potential gradient across a membrane leads to a migration of charged components.

The mass transport in the various membrane processes can be described by the phenomenological equations which can be simplified by certain approximations that are based on postulating certain membrane models such as the

solution-diffusion model, the porous membrane model, and the ion-exchange membrane model.

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Matrimid® Membranes

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Matrimid membrane can be developed from different types of commercially available polyimide resins such as Matrimid 5218 (3,3',4,4'-benzophenonetetracarboxylic dianhydride and diaminophenylindane), Kapton, Matrimid 5292A (4,4-bismaleimidodiphenylmethane), Matrimid 5292B, Matrimid P84, and Matrimid 9725 (micropulverized version Matrimid 5218) (www.ciba.com; www.huntsman.com). The employment of commercially available polyimide resin was found to be more practical from the economic point of view due to the high cost of synthesized polyimides on the laboratory scale (Xiao et al. 2005).

The Matrimid membranes are commonly prepared via solvent evaporation (Sridhar et al. 2007; Mosleh et al. 2012) and phase inversion (Basu et al. 2010) techniques. The asymmetric (Nistor et al. 2008; Basu et al. 2010) or dense (Shishatskiy et al. 2006) Matrimid membrane can be in flat sheet (Shishatskiy et al. 2006; Aziz and Ismail 2010) or hollow fiber (Dong et al. 2011; Ding et al. 2008; Jiang et al. 2004) form.

Matrimid especially the Matrimid 5218, an extremely popular polyimide, has been extensively studied for gas separation, pervaporation processes, and carbon membrane due to the combination of relatively high gas permeability coefficients and separation factors as well as excellent mechanical properties, high solubility in non-hazard organic solvents, and high glass transition temperature in comparison to polycarbonate, polysulfone, and other materials (Wind 2002; Nistor et al. 2008). The typical permeation properties of Matrimid 5218 are tabulated in Table 1.

The overall performance (in terms of permeability and selectivity) of Matrimid membrane in gas separation processes can be diverse as reported in the open literatures which was due to the several factors such as:

- (i) Operating conditions of gas permeation test
- (ii) Effective (skin layer) membrane thickness (the thinner the selective skin layer is, the better the gas flux will be)
- (iii) Membrane morphology as a consequence of the different conditions of phase inversions of membrane preparation technique
- (iv) Properties of the gas tested

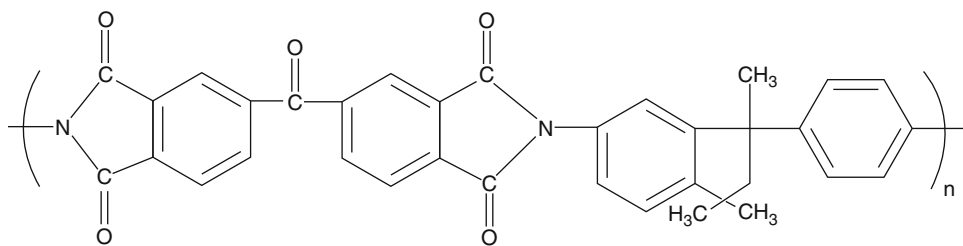
Matrimid® Membranes, Table 1 Typical permeation properties of Matrimid 5218 (David et al. 2011)

Permeability of pure gases (Barrer ^a)		Ideal selectivity
PO ₂	P _{N2}	O ₂ /N ₂
1.32–1.34 ^b	0.185 ^b	7.2 ^b

^a1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² S⁻¹ cmHg⁻¹ = 7.5×10^{-18} m³ (STP) m m⁻² S⁻¹ Pa⁻¹,

^bPure gas Permeation measurement for O₂ and N₂ at 3447.3785 kPa, 25 °C

The weakness of Matrimid membrane is always pronounced by the membrane transport properties that are strongly affected by the gas separation operating conditions such as pressure and temperature that are likely relied to the changes in density, and consequently in the free volume, of the polymer itself (Rowe et al. 2009; David et al. 2011). Hence, the presence of minor components in the feed flow, such as impurities or water vapor, can strongly affect the gas transport mechanism, thus altering the separation performances (Chen et al. 2011). Moreover, its glassy nature may lead to plasticization phenomena at high fugacity of gases and vapors and to aging phenomena that decrease the performances upon time (Tin et al. 2003). These shortcomings limit the Matrimid membrane application particularly in gas separation processes. Due to this awareness, numbers of modification have been reported by researchers to improve the Matrimid membrane properties in order to fulfill the gas separation performance requirement particularly to surpass the Robeson boundary line (Basu et al. 2010). The idea to modify the Matrimid membrane was initiated by the good processability of the polymer itself owing to its carbonyl functional groups (see Fig. 1) that may lead to the donation of electrons to form good interaction with certain electron acceptors (Chung et al. 2003). The modifications were conducted on the Matrimid membrane including the incorporation of mesoporous silica molecular sieve (Kenneth et al. 2002), bromination (Guiver et al. 2002; Xiao et al. 2005), blending with other polymers (Chung et al. 2003), thermal treatment (Krol et al. 2001), and chemical cross-linking (Tin et al. 2003).



Matrimid® Membranes, Fig. 1 Chemical structure of Matrimid

Due to the excellent properties shown by Matrimid membrane, which is desirable for gas separation process, therefore it is worth to accelerate relevant modifications on this promising membrane for better separation performance.

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Mechanical Cleaning

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Synonyms

Physical cleaning

Mechanical cleaning of membranes may be used for the removal of fouling, particularly if other common utilized cleaning practices based on chemical and hydraulic methods do not restore membrane flux. Sustainable membrane performance is hampered by complex fouling phenomena, which occur on the membrane surface or inside the pores, leading to a reduction in productivity and an increase in transmembrane pressure (TMP). Cleaning of the membranes, irrespective of the procedure used, has a knock-on effect to the membrane life expectancy and operational replacement costs (Van der Roest et al. 2002).

The methods used depend upon the separation process and the configuration of the module. The most important aspect during the operation of membranes is to prevent the forming of a cake layer i.e., deposits on the membrane surface. Cake layer formation is predominantly caused by concentration polarization occurring in the liquid boundary layer in front of the membrane. Mechanical cleaning is accomplished by introducing high shear forces at the membrane surface by mechanical action in order to loosen and dislodge the deposits. In general, the mechanical action in membrane systems is provided by using various materials, turbulence promoters e.g., scouring sponge balls or fluidized particles. One of the benefits of using turbulence promoters is that this method does not involve any significant loss in water production during the membrane cleaning.

Sponge balls, made typically of polyurethane foam, are commonly used for cleaning of tubular membrane systems, when treating wastewater and industrial process water, due to their size limitation (Psoch and Schiewer 2006). Sponge balls are typically slightly larger (1–2 mm) than the inner diameter of membrane tubes to ensure an effective scouring of accumulated deposits from the membrane surface. The cleaning action of membrane is obtained by forcing sponge balls down the tubes at high velocity by the application of fluid pressure. Sponge balls are either injected directly to the feed stream and then collected from the retentate using appropriate mesh screens, or are automatically pushed back and forth along the tubes from storage channels on both the inlet and outlet of the module (Scott 1995). The mechanical cleaning by sponge balls can be performed in online and/or offline modes. However, the online mode is more practical as the cleaning process can take place while the plant is in operation, so that this method does not involve any significant loss in water production during the membrane cleaning. The cleaning frequency is much higher, thus the tubes are maintained clean at all times. Mechanical cleaning by sponge balls is most effective at removing soft biological and organic foulants from the membrane surface but not from within the membrane pores (Zeman and Zydney

1996). Sponge ball cleaning has also been combined with chemical cleaning successfully restoring flux (Ebrahim 1994). The removed deposits are gradually disposed of via the waste stream to the local water course. There are many manufacturers of sponge cleaning balls such as Luxx Ultra-Tech Inc., Taprogge, Technos, Water Science of America (WSA), Remington and Schmitz. Several different types of sponge balls i.e., standard, extended life, or abrasive in a variety of hardnesses and sizes are available commercially. Whereas the standard balls are designed for general application, the expanded life balls are only applied for mild fouling problems. The extended life balls are coated with thin smooth skin, which wears out slowly resulting in extended life. Abrasive balls are coated fully or partially with carborundum and are designed for abrading hard deposits in metal tubes only. After being used, sponge balls should be washed out to remove contaminants, thus increasing the longevity of the balls (Web Source). The fouling removal ability of sponge balls depends on many factors such as size, number, hardness, surface texture and age of the balls, the frequency and duration of treatment, and nature of fouling.

In order to select the most appropriate sponge balls the following criteria for ball assessment can be considered (Mustafa Osman Ahmed Hamed et al. 2001):

- Mechanical damage (ball splitting) is caused by the collision of balls with the flow path surfaces. The repeated compression of the balls also leads to mechanical damage by erosion and peeling.
- Shrinking is mainly attributed to the ball material and its temperature tolerance and can be measured by its size and weight.
- Surface wear, which occurs by abrasion due to the deposits in the tubes, is a common phenomenon resulting in loss of ball effectiveness.
- Deformation in the shape of the balls is mainly related to the temperature and pressure tolerance of the balls' material and results in uneven tube cleaning.
- Loss of texture is a major deficiency of balls that restricts the ability of balls to regain their

shape and size. It also results in sticky balls. Ball material should be good enough to withstand higher temperatures and prolonged contact with seawater.

Fluidized particles (glass/steel beads, foam cubes, Kaldnes[®] and Rauschert carriers, granulates). The use of fluidized particles minimize or control concentration polarization and membrane fouling through the enhancement of the convective flow and the generation of turbulences due to the introduction of fluidized particles in the flow conduit or membrane tank. Moreover, fluidized particles continuously mix up the liquid boundary layer in front of the membrane and scour the membrane surface, thereby, preventing membrane fouling and also remove the matter that has already been deposited.

Fluidized glass ($\rho = 2900 \text{ kg/m}^3$) and steel beads ($\rho = 7800 \text{ kg/m}^3$) with diameter ranging from 0.46–1.04 mm to 1.0–2.0 mm, respectively, were successfully applied for cleaning of the tubular polysulfone membranes. Smaller and lighter beads seem to improve permeate flux through the membrane significantly, minimizing the risk of membrane damage (Noordman 2000). Moreover, the use of fluidized particles seems to be especially attractive for liquids with higher viscosity as the risk of membrane damage is reduced with increasing velocity.

Another mechanical cleaning procedure, using polyurethane foam cubes or polyethylene Kaldnes[®] or Rauschert (Bioflow 9) carriers can be applied for membrane bioreactors (MBRs). A MBR process is the combination of a conventional activated sludge process and membrane filtration and is now widely used for municipal and industrial wastewater treatment. The cleaning elements are introduced into filtration tanks equipped with submerged flat sheet membranes to swirl between the membrane sheets and clean them during filtration. MBR operation using of foam cubes with a size of 3–5 mm and polyethylene Kaldnes[®] and Rauschert (Bioflow 9) carriers of 9–10 mm partly removes membrane fouling, thereby increasing the membrane's performance. The use of the cleaning elements, with a 20 %

filling volume of the filtration tank, led to a 35 % increase in filtrate production (Wulf and Orth 2008). One disadvantage of using this cleaning method is that the introduced carriers may damage the membrane and another one is the requirement of big enough gaps between membrane plates (>10 mm), so that the cleaning elements can freely move. Such big gaps between membrane plates are directly related to a lower packing density of membranes, which leads to larger foot print and thus higher costs.

Another novel mechanical cleaning strategy, based on the use of plastic granulates, was developed for continuous cleaning of BIO-CEL[®] modules of Microdyn-Nadir, Germany (company's website) which incorporates the required constructional and hydraulic characteristics (Siembida-Lösch 2011). The mechanical cleaning process using granular material is operated in a loop reactor without interrupting filtration and permeate loss. The process is being supported by the crossflow aeration system and the use of plastic granulates. Granulates, introduced directly into an activated sludge filtration tank, flow upward alongside the membrane forced by the crossflow air. Granulates are returned to the base of the module with the downstream water flow outside the membrane modules where it enters again into the upstream flow. Thereby continuous removing of the cake layer occurs. Granulates are retained in the filtration tank during sludge discharge by suitable sieving systems. Granulates must meet some requirements, to efficiently clean the membranes, i.e.,

- Nonporous, to prevent from the change of density during operation by taking up water and forcing material to settle
- Density >1 kg/L to move freely with the liquid flow in the reactor
- Size <5 mm, as the gap between two BIO-CEL[®] membrane sheets is 8 mm
- Form should be either globular or oval without edges to prevent the damage of membrane material
- Biologically inert, to prevent microbial degradation

The most appropriate specific aeration demand per membrane area (SADm) for the granular material of being moved into the loop is $0.7 \text{ m}^3/(\text{m}^2 \cdot \text{h})$. Operation at higher or lower SADm values can lead to irregular distribution of granulates or to settling in a filtration tank, respectively. Typically, a granulate concentration of 4 kg per m^3 of activated sludge volume is sufficient for an optimal MBR operation treating municipal wastewater, however, it can vary for other applications (Siembida-Lösch 2011). The patented process BIO-CEL[®] MCP (Mechanical Cleaning Process) reduces operating costs as it enables much higher specific flows. This lowers investment costs (smaller membrane area needed) and reduces energy consumption (crossflow) for the entire system. Furthermore, the MCP is suitable for external module cleaning if already fouled and also minimizes chemical demand. The fouling layer formed during the filtration process can be removed safely without causing any damage to the membrane.

Cross-References

- Fouling
- Membrane Bioreactor
- Retentate

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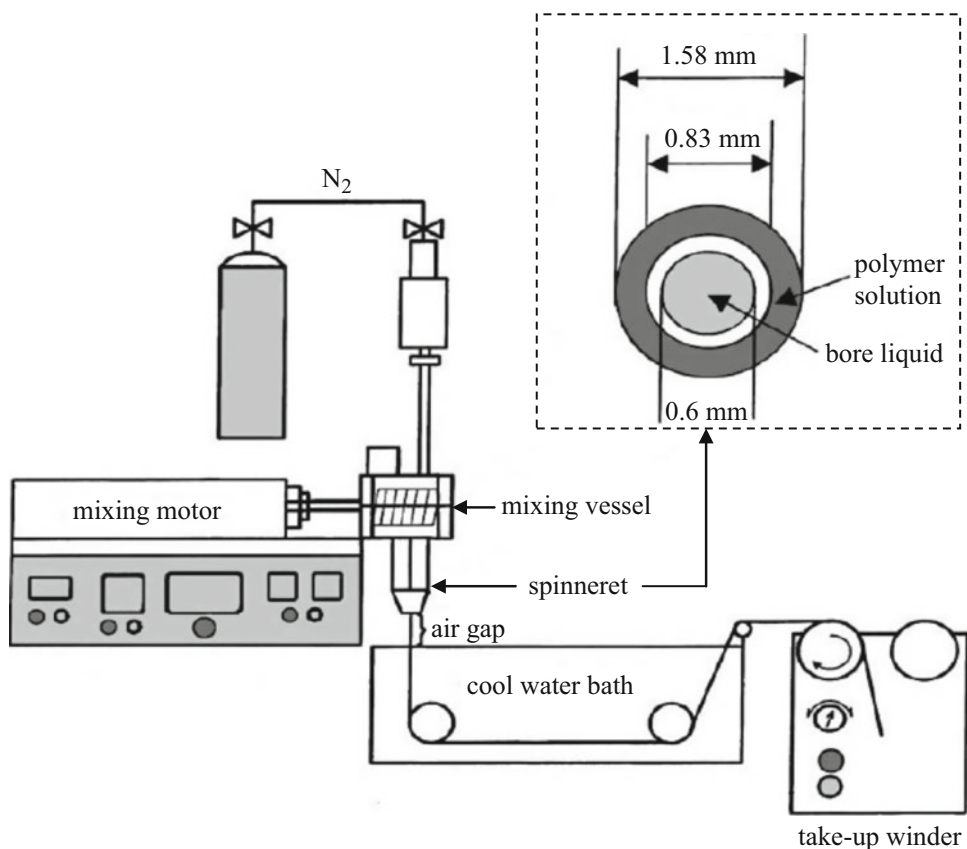
Melt Spinning

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Melt spinning is a fiber fabrication technique from polymers or polymer/diluent systems that can be melted. Both fibers (filaments) and hollow fibers can be prepared by melt spinning technique. The polymer is first compressed, heated, and melted by an extrusion screw, then forced to pass through a spinneret of different geometries. The polymer solidifies by cooling (thermal precipitation) after being extruded from the spinneret and then collected by means of take-up wheels. The spinning rate in melt spinning (thousands of meter per minute) is much higher than that used in the dry/wet spin technique (meters per minute) (Mulder 1992).

It is possible to prepare both porous and nonporous hollow fibers by thermal precipitation also known as thermally induced phase separation (TIPS). Figure 1 shows a typical example of the systems used (Khayet and Matsuura 2011; Matsuyama et al. 2003). A given amount of a dope solution (polymer/diluent system) is mixed under a nitrogen atmosphere in the vessel heated at a temperature above the melting temperature of



Melt Spinning, Fig. 1 Schematic diagram of a hollow fiber preparation system via thermally induced phase separation (TIPS) technique (Reprinted from (Matsuyama et al. 2003). Copyright 2003, with kind permission from Elsevier)

the blend. The homogeneous polymer/diluent melt blend is then fed to a spinneret by a gear pump under nitrogen pressure of about 0.2 MPa. The spinneret shows an outer and an inner tube. A diluent can also be introduced into the inner tube of the spinneret to make a lumen of the hollow fiber. The fiber extruded from the spinneret enters in the water bath under a controlled temperature to induce phase separation and solidification by means of polymer crystallization. Simultaneously, the nascent fiber is wound by using a take-up winder at several speeds. The diluent present in the fiber is then following different methods that depend on the type of the diluent. Other than the dope solution, the variables involved in hollow fiber membrane preparation

via the TIPS technique are the air gap distance, which is the distance from the spinneret to water bath or to take-up wheels, the spinning temperature, the water bath temperature, the take-up speed, the spin draw ratio, the extrusion rate of the blend, the flow rate of the diluent in the inner tube of the spinneret, the cold stretching through the air gap, the temperature of the polymer/diluent blend and its composition, etc.

The TIPS technique is caused by a temperature change and typically consists of the following basic steps (Khayet and Matsuura 2011; Lloyd 1990):

- i. A homogeneous solution is first formed by melt blending a polymer and a liquid or solid

having a low molecular weight and a high boiling point, referred to as the diluent (i.e., does not cause dissolution or swelling of the polymer at room temperature). The initial temperature must be less than the boiling point of the diluent and is typically 25–100 °C greater than the melting temperature or glass transition temperature of the polymer. The polymer must be stable at this initial temperature. To avoid confusion, the term diluent will be used instead of solvent, hereafter. The diluent acts as a solvent only when it can dissolve all polymers. When the solvent power decreases sufficiently so that liquid-liquid demixing takes place, the term solvent is not appropriate anymore.

- ii. The hot solution is extruded or spun in the desired shape including a hollow fiber.
- iii. The solution is cooled at controlled rate or quenched to induce phase separation and solidification.
- iv. The diluent(s) that is trapped in the polymer matrix during phase separation and solidification is removed by solvent extraction procedure.
- v. The extractant is removed by evaporation to yield microporous structures if required.
- vi. Posttreatment processing might be applied to improve the desired separation characteristics of the TIPS membrane. Stretching might be included in this step.

TIPS can be applied to a wide range of polymers, including those that cannot be otherwise formed into membranes because of poor solubility in solvent.

The type of phase separation (liquid-liquid phase separation, solid-liquid phase separation, combined liquid-liquid and solid-liquid phase separation) that is likely to occur for a given system (composition and temperature) is indicated by the phase diagram (Khayet and Matsuura 2011; Laxminarayan et al. 1994). This is a useful tool explaining the morphology and bulk structure of TIPS membranes. Polymers such as polyethylene (PE), polypropylene (PP), and poly(2,6-dimethyl-1,4-phenylene ether) (PPE) were used in melt spinning (Khayet and Matsuura 2011).

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Membrane (Definition, Function, Structure)

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Synonyms

[Membrane classification](#); [Membrane definition](#); [Membrane function](#)

A precise and complete definition of a membrane that covers all its aspects is rather difficult, even when the discussion is limited to synthetic structures. Various definitions have been reported in the literature, most of them focusing on the

selective properties of the membrane. For example, Lonsdale defined a synthetic membrane as an interphase that separates two phases and restricts the transport of various components in a specific manner (Lonsdale et al. 1982). In new membrane processes, such as membrane contactors, the membrane is a nonselective barrier that separates and contacts two adjacent phases. Therefore, in the most general sense, we can define a membrane as a discontinuous phase between two adjacent phases that permits the exchange of matter, energy, and information between the phases with selective or nonselective properties.

Separation of a mixture in a membrane process is the result of different transport rates of different components through the membrane. The transport rate of a component through a membrane is determined by driving forces such as concentration, pressure, temperature, and electrical potential gradients, as well as by the concentration and mobility of the component in the membrane matrix.

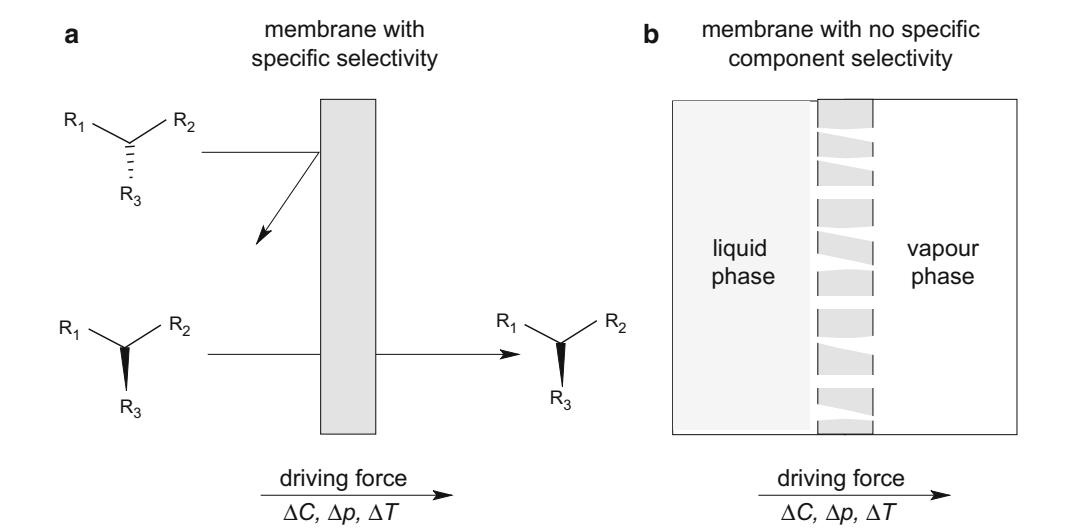
A membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure (Strathmann et al. 2006). It may be solid or liquid and may consist of organic, inorganic, or biological materials as well as a mixture of them. Membranes made of inorganic components dispersed in the organic matrix are called mixed matrix membranes. Membranes made of biological components contained in organic or inorganic materials are called biohybrid membranes. When membranes are engineered with materials that transfer principles from biology, they are termed biomimetic membranes. Bioinspired membranes are a broader term compared to biomimetic. They are synthetic membranes that mimic the structure and function of their natural counterpart. A biomimetic membrane is also bioinspired, but not necessarily the other way round.

A membrane may be neutral or it may carry positive or negative charges, or functional groups with specific binding or complexing abilities. Its thickness can be less than 100 nm to more than a millimeter. The electrical resistance may vary from more than $1,000,000 \Omega \text{ cm}^2$ to less than $1 \Omega \text{ cm}^2$.

The term “membrane,” therefore, includes a great variety of materials and structures, and a membrane can often be better described by its

function rather than by its structure. Some materials, such as protective coatings or packaging materials, show typical membrane properties and are in fact membranes. Most materials functioning as membranes have the characteristic property in common of restricting the passage of different components in a very specific manner. In some cases, they may restrict the passage of the same component, depending on the state: a hydrophobic polymeric membrane may allow the passage of water as vapor phase but not as liquid phase, as, for example, in membrane distillation. In other cases, e.g., membrane contactors, the porous structure of the membrane material functions as a barrier that keeps in contact two adjacent phases between which a mass transfer occurs and separates them at the same time. In this case the membrane has no direct effect on the transport of various components and is nonselective toward the passing species. The concept of a selective and nonselective membrane is illustrated in Fig. 1 which shows (a) a membrane which is highly selective and capable of separating, e.g., two enantiomers, and (b) a membrane that acts as a barrier between two phases and avoids the mixing of the phases but has no selective properties related to the transport of different components from one phase to the other.

A porous structure represents a very simple form of a membrane, which closely resembles the conventional filter as far as the mode of separation is concerned. These membranes consist of a solid matrix with defined holes or pores which have diameters ranging from less than 1 nm to more than $10 \mu\text{m}$. The macromolecular size of the species to be separated plays an important role in determining the pore size of the membrane to be utilized and the related membrane process. Porous membranes with average pore diameters larger than 50 nm are classified as macroporous, and those with average pore diameters in the intermediate range between 2 and 50 nm are classified as mesoporous. Membranes with average pore diameters between 0.1 and 2 nm are classified as microporous. Dense membranes have no individual permanent pores, but the separation occurs through fluctuating free volumes, by solution-diffusion mechanism (Strathmann et al. 2010).



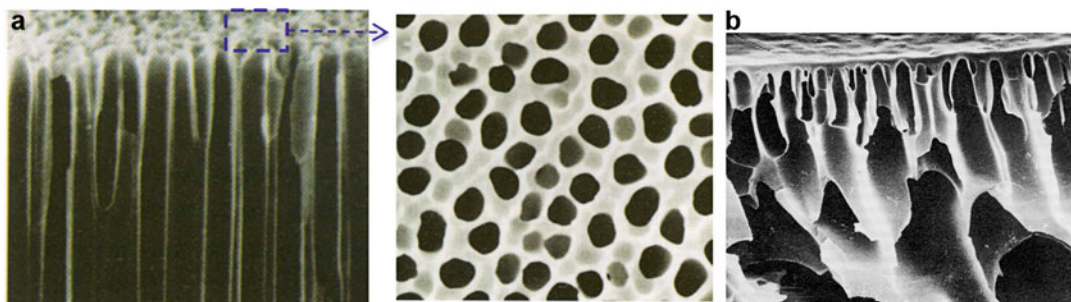
Membrane (Definition, Function, Structure), Fig. 1 Schematic drawing illustrating (a) a membrane which is selective for the transport of different components such as two enantiomers and (b) a membrane which separates a liquid and a vapor phase and allows passage of vapor molecules but is not selective for the transport of different components

Membrane type	non-porous	micro-porous	meso-porous	porous		
Membrane process	reverse osmosis gas separation pervaporation	nanofiltration	ultrafiltration	microfiltration		
Pore or particle size	0,1 nm	1 nm	10 nm	0,1 μm	1 μm	10 μm
Separated components	gases vapours	sugars	proteins	bacteria	emulsions	colloids

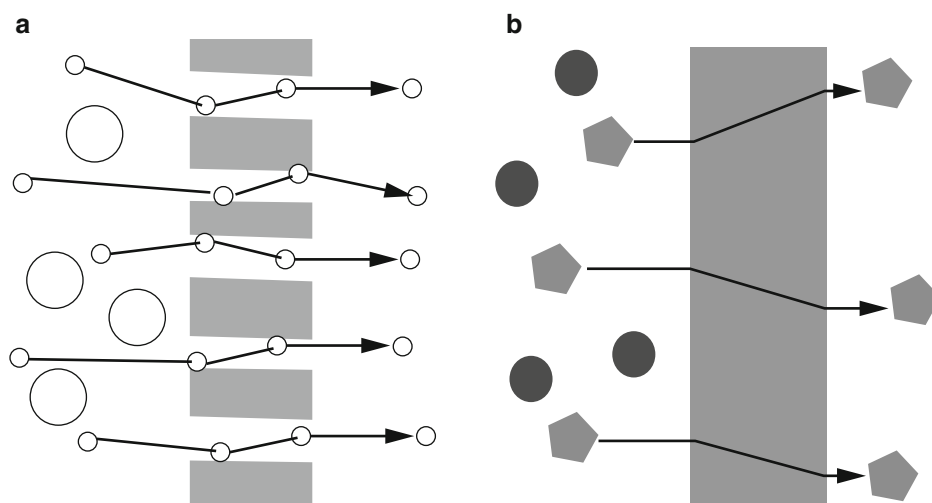
Membrane (Definition, Function, Structure), Fig. 2 Schematic classification of membranes, related processes, and separated components

The schematic representation of such classification is illustrated in Fig. 2.

In pressure-driven membrane processes, the separation of the various components is achieved by a sieving mechanism with the pore diameters and the particle sizes being the determining parameters. In thermally driven membrane processes, the separation is based on the principle of



Membrane (Definition, Function, Structure), Fig. 3 Porous symmetric (a) and asymmetric membrane (b)



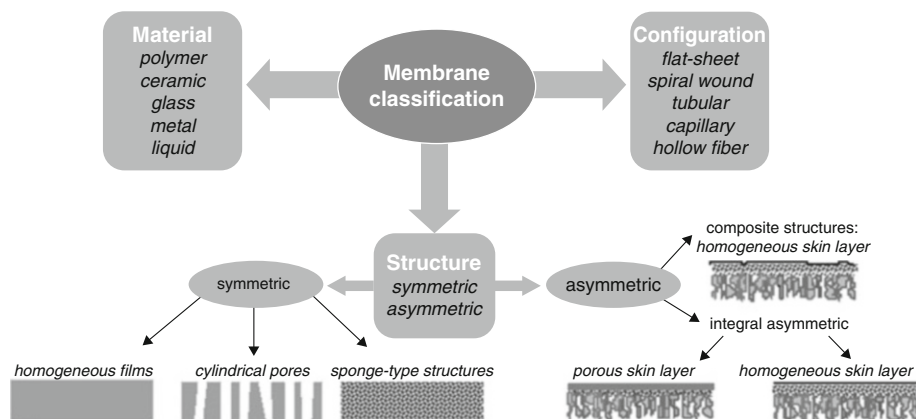
Membrane (Definition, Function, Structure), Fig. 4 Schematic diagram illustrating (a) the sieving mechanism of a porous membrane and (b) the solution-diffusion mechanism in a nonporous membrane

phase equilibrium, and the non-wettability of membrane pores is the determining parameter. Membrane structure may be symmetric (Fig. 3a), i.e., the pore diameters do not vary over the membrane cross section, or they can be asymmetric (Fig. 3b), i.e., the pore diameters increase from one side of the membrane to the other typically by a factor of 10–1,000.

The mechanism by which certain components are transported through a membrane can also be very different. In some membranes, for example, the transport is based on viscous flow of a mixture through individual pores of the membrane caused by a hydrostatic pressure difference

between the two phases separated by the membrane. This type of transport is referred to as *viscous flow*. The components that permeate through the membrane are transported by convective flow through macropores under a pressure gradient as driving force and the separation occurs because of size exclusion as indicated in (Fig. 4a). Darcy's Law describes this type of transport. It is the dominant form of mass transport in micro- and ultrafiltration but also occurs in other membrane processes.

If the transport through a membrane is based on the solution and diffusion of individual molecules in the nonporous membrane matrix due to a



Membrane (Definition, Function, Structure), Fig. 5 General classification of membranes

concentration or chemical potential gradient, the transport is referred to as *diffusion*. The separation occurs because of different solubility and diffusivity of components into the membrane material as indicated in (Fig. 4b).

Fick's law describes this type of transport. The diffusion of molecules through homogeneous dense membranes occurs through the free volume elements, or empty spaces between polymer chains caused by thermal motion of the polymer molecules, which fluctuate in position and volume on the same time scale as the molecule permeates. The transition between fluctuating free volumes and individual permanent pores is controversial. In general it is considered in the range of 5–10 Å in diameter.

This form of mass transport is dominant in reverse osmosis, gas separation, and pervaporation but it may occur in other processes, too.

If an electrical potential gradient across the membrane is applied to achieve the desired transport of certain components through the membrane, the transport is referred to as *migration*. Migration occurs in electrodialysis and related processes and is limited to the transport of components carrying electrical charges such as ions.

The general classification of membranes, on the basis of material, structure, and configuration, is illustrated in Fig. 5.

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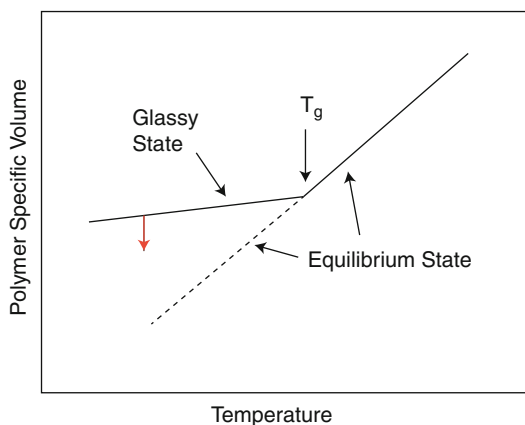
Membrane Aging

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The term **membrane aging** as used here refers to the physical aging process that occurs over time for a membrane based on a glassy polymer. As polymers are cooled through the region of the glass transition temperature, T_g , the time scale of motions of the polymer chain segments becomes much longer than the time scale of the observation; thus, the material is no longer able to maintain an equilibrium structure like it does above T_g . Thus, glassy polymers exist in a nonequilibrium state that has a higher specific volume (or lower

density) than it would have if it could have maintained an equilibrium state. This situation is illustrated in Fig. 1 that shows a plot of polymer-specific volume versus temperature. The actual state achieved below T_g depends on how the glass was formed and all its prior history. The extra fractional free volume, FFV, the glass has owing to being trapped in this nonequilibrium



Membrane Aging, Fig. 1 Illustration of the specific volume versus temperature *above* (rubbery state) and *below* (glassy state) the glass transition temperature of a polymer. The arrow indicates the path of slow densification of the glass over time

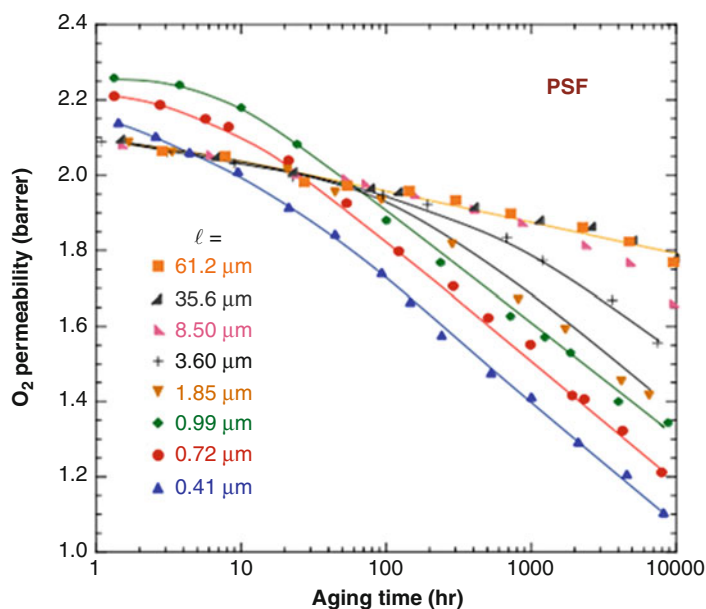
state affects many properties such as gas permeability, P , as seen by the relationship:

$$P = Ae^{-B/FFV} \quad (1)$$

At temperatures below T_g , the material continues to proceed toward its equilibrium (see arrow in Fig. 1), albeit at a very slow rate. This densification process is called physical aging or structural relaxation (Kovacs et al. 1977). This process of aging is thermally reversible meaning that the original state can be restored by heating above T_g . As a result of this densification process or physical aging, all properties like permeability also evolve over time.

It has been observed that the rate of physical aging of glassy polymer films depends strongly on thickness and that this effect is particularly pronounced below thicknesses of less than about $1 \mu\text{m}$, which can be tracked by measuring gas permeability, as seen in Fig. 2 for polysulfone (Huang and Paul 2004). A convenient summary of the experimental techniques used to study these effects of thickness for thin films and contemporary interpretations of the observations has been given by Rowe et al. including the effects of prior history (Rowe et al. 2011).

Membrane Aging, Fig. 2 Effect of physical aging on the oxygen permeability for a series of polysulfone films (at 35°C) (Huang and Paul 2004) (Reproduced with permission of Elsevier (Copyright 2004))



Since gas separation membranes must have a very thin, thicknesses ~ 100 nm, skin or separating layer to achieve high fluxes, they are expected to exhibit similar effects when the polymer is glassy. This may be manifested as a decline in productivity over the lifetime of the module. Of course, much of this aging may have already occurred prior to the membrane being put into service. Even so, this means that the actual permeability of the active layer may be much lower than estimated by thick film (tens of microns in thickness) tests.

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Membrane Air Dehydration

► Air Dehydration by Membrane Technology

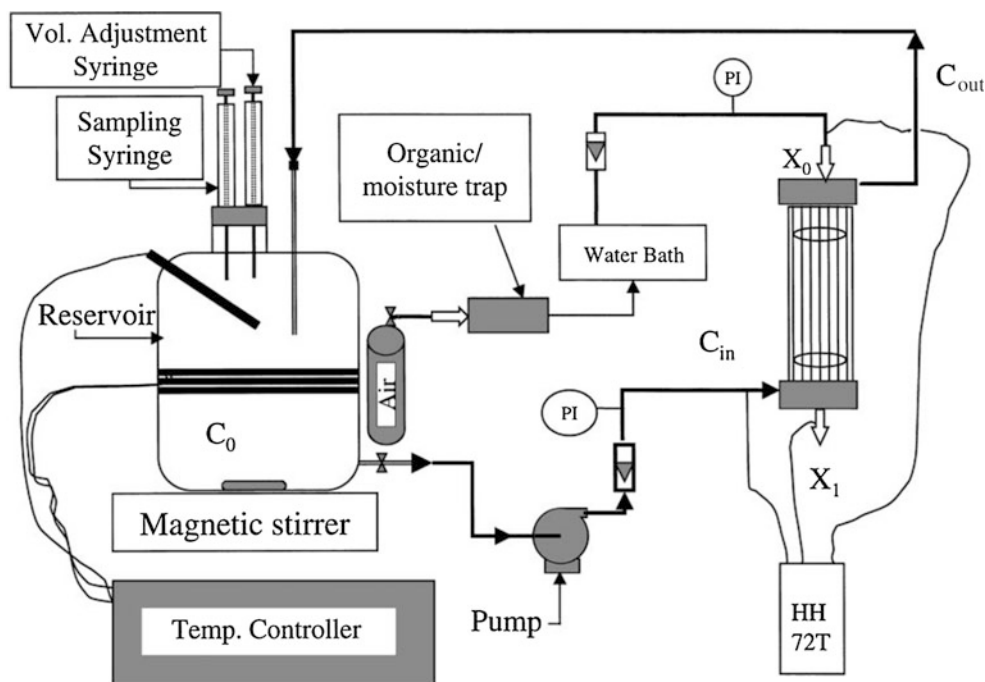
Membrane Air Stripping (MAS) Process

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Contamination of groundwater and wastewater by volatile organic compounds (VOCs), resulting from improper disposal, poses a serious

environmental problem in many areas. Among several methods of removing VOCs, air stripping appears to be the best available technology. However, this method has limitations in term of fouling, larger footprint, and higher capital costs. Recovery of VOCs from water by membrane air stripping (MAS) is an alternate process with a lot of potential (Mahmud et al. 1998). Due to higher surface-to-volume ratio of the hollow fiber membranes, this is the desired format where contaminated water is pumped through the lumen side of the fiber while dry air is passed over the shell side of fibers. Although the overall mass transfer coefficient in MAS is lower than the spray towers but overall volume specific rate of stripping is several times higher in MAS due to higher surface-to-volume ratio. Mass transfer resistances in MAS processes have been studied by many researchers. Semmens et al. (1989) reported individual local liquid phase, local gas phase, and membrane mass transfer resistances for the MAS process using L  v  que (1928) correlations. It was noted that the predicted overall mass transfer coefficient was significantly higher than the observed values. Membrane resistance for polypropylene fibers depended on wetting of pores (Malek et al. 1997). The mass transfer resistance due to the membrane in pure water and aqueous solution containing VOCs were investigated at different airflow values for developing a process. It was found that extent of air or water in the pores contributes to the final resistance. The models were built by considering resistance to the partially air-filled pores. The model prediction agreed well with literature and our own laboratory data for a variety of VOCs (Mahmud et al. 2000, 2002, 2004). Further, there was no significant effect of the initial concentrations of VOCs in water. Based on the above analysis, a laboratory scale study of removal of naphtha components from wastewater showed that up to 92 % of original naphtha could be removed by MAS process (Fig. 1). It was also observed that overall mass transfer coefficients and propensity of stripping depended on the structure of individual naphtha components (Mahmud and Kumar 2012).



Membrane Air Stripping (MAS) Process, Fig. 1 Membrane air stripping experimental setup

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Membrane Artificial Organs

Loredana De Bartolo

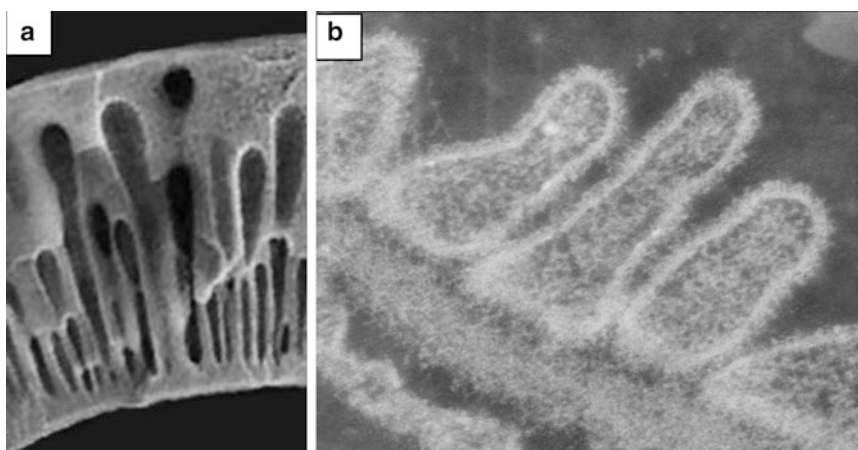
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Synonyms

[Artificial functional organ](#)

Membrane artificial organs are membrane devices that replace the function of natural organs like artificial kidneys/dialyzers and artificial lungs/blood oxygenators for the purpose of restoring the specific organic functions.

Polymeric semipermeable membranes and membrane processes play a pivotal role in replacement therapy for acute and chronic organ failure and in the management of immunological disease (De Bartolo and Drioli 1998).



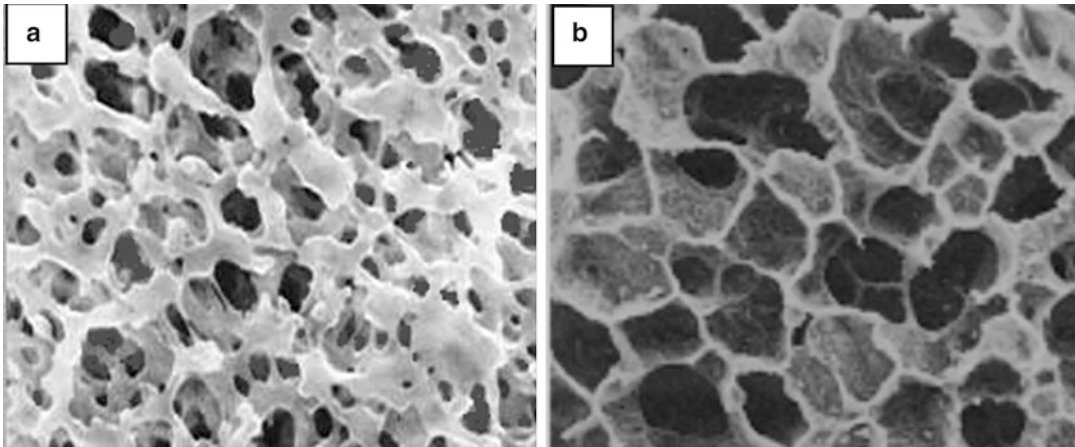
Membrane Artificial Organs, Fig. 1 Comparison of hemodialysis polyethersulfone membrane (a) with glomerular membrane (b)

In these devices semipermeable membranes act as selective barriers for the removal of endogenous and exogenous toxins from patient's blood (hemodialysis, hemofiltration, etc.) or for gas exchange with blood (blood oxygenation) (Kawakami 2008). Hemodialysis is an extracorporeal treatment of patients affected by kidney failure. The treatment is intermittent, generally three times weekly for periods between 3 and 5 h depending upon the patient clinical requirements. In hemodialyzer, selective membranes play the same function of kidneys allowing the extracorporeal removal of waste products such as creatinine and urea and free water from the blood when the kidneys are in a state of renal failure. It involves diffusion of small solutes across the semipermeable membrane retaining protein and molecules with high molecular weight. Membranes used in the hemodialyzer device have been engineered in order to have the similar structure of the renal glomerular membrane to ensure a similar performance. Membrane hollow fiber and glomerular capillary employ a cylindrical cross section in order to minimize perimembrane boundary layers and to maximize transport efficiency, have same ratio of wall thickness/cross-sectional diameter, and are composed of linear hydrophilic polymers that rely on van der Waals forces and islands of crystallinity to retain their integrity. Difference is scale: the glomerule has a

diameter of 4–8 μm , and synthetic hollow fiber membranes have diameters in the range of 200 μm . For example, the structure of polyethersulfone membrane that is widely used in hemodialyzer is similar to glomerular membrane. Both have asymmetric structure with a selective skin layer supported by a sponge layer (Fig. 1). This structure confers to the membrane an optimal selectivity and high mechanical resistance.

The first hollow fiber hemodialyzers made of unmodified cellulose were used clinically in the 1960s. Since the first cellulose membranes, significant efforts have been focused on the development of more biocompatible and selective membranes with respect to the clearance of “middle” molecules like β_2 -microglobulin that is known to be associated with many dialysis-related disorders. A variety of synthetic polymers and modified cellulosic materials including polysulfone (PSF), polyethersulfone (PES), polyamide (PA), polyacrylonitrile (PAN), cellulose triacetate (CTA), and hemophan (HP) have been used for preparing hemodialysis membranes (Humes et al. 2006; Su et al. 2008).

Extracorporeal blood oxygenators are used to oxygenate the blood during open-heart surgery. Today, the vast majority of these blood oxygenators use hydrophobic microporous hollow fiber membranes to separate the blood and gas phases.



Membrane Artificial Organs, Fig. 2 Comparison of oxygenator polypropylene membrane (a) with pulmonary alveoli (b)

Oxygen diffuses from the gas phase through the gas-filled membrane pores into the blood. Oxygen in the blood plasma binds to hemoglobin present in the red blood cells. Consequently the rate of oxygen transfer is enhanced compared to the oxygenation of water where the oxygen does not react in the liquid phase (Lewandowski 2000).

Membrane oxygenators in current use utilize microporous, silicon, or polypropylene membranes. Currently, there are three principal types of oxygenator: (a) Plaque oxygenators are built with microporous membranes of expanded polypropylene, folded in a Z shape. In these apparatuses, blood and gas flow in opposite sides of the membrane. (b) Spiral oxygenators utilized silicon membranes that are rolled around a central axis. (c) Hollow fiber oxygenators are manufactured with microporous polypropylene membranes, constituted by hollow fibers or capillary. This is the most common type of oxygenator used currently.

The most common membranes for blood oxygenator have been engineered in order to have morphology close to the pulmonary alveoli. For example oxygenator polypropylene membranes have massive reticulated surfaces deployed as fine, porous, open-cell foams, which remind the saccular form of the alveoli and the very thin alveoli septa (Fig. 2). In the natural lung, blood flows through fine capillaries in the alveoli and exchanges O_2 and CO_2 across a barrier made up of

capillary endothelial cells; in oxygenators blood flows on the outside of a large bore fiber, with diameter of 300 μm , and exchanges respiratory gases across a meniscus that forms across the membrane pore at the interface of blood and gas.

The diffusion of these gases inside the oxygenator depends on the type of material of the membrane and on its thickness and porosity, but it is also influenced by the thickness of the layer of blood in contact with the membrane and by the characteristics of the blood flow (Wickramasinghe et al. 2005).

Cross-References

► [Acute Kidney Injury \(AKI\)](#)

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Membrane Based Solvent Extraction

Lidietta Giorno

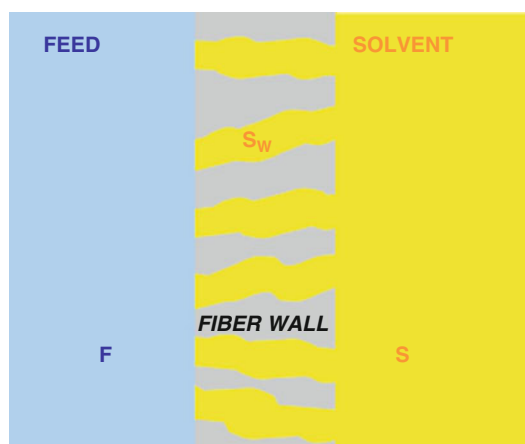
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Synonyms

Liquid-liquid membrane extraction

In membrane based solvent extraction (MBSE) two immiscible phases are in contact with a porous membrane. One of the two phases wets the membrane whilst the other does not wet it (Fig. 1).

In membrane-based solvent extraction mass-transfer between two immiscible solvents occurs



Membrane Based Solvent Extraction, Fig. 1 Schematic of MBSE mechanism at membrane level. F: feed, S: solvent, Sw: solvent in fiber wall. Here is shown the case where the membrane is wetted by the organic solvent

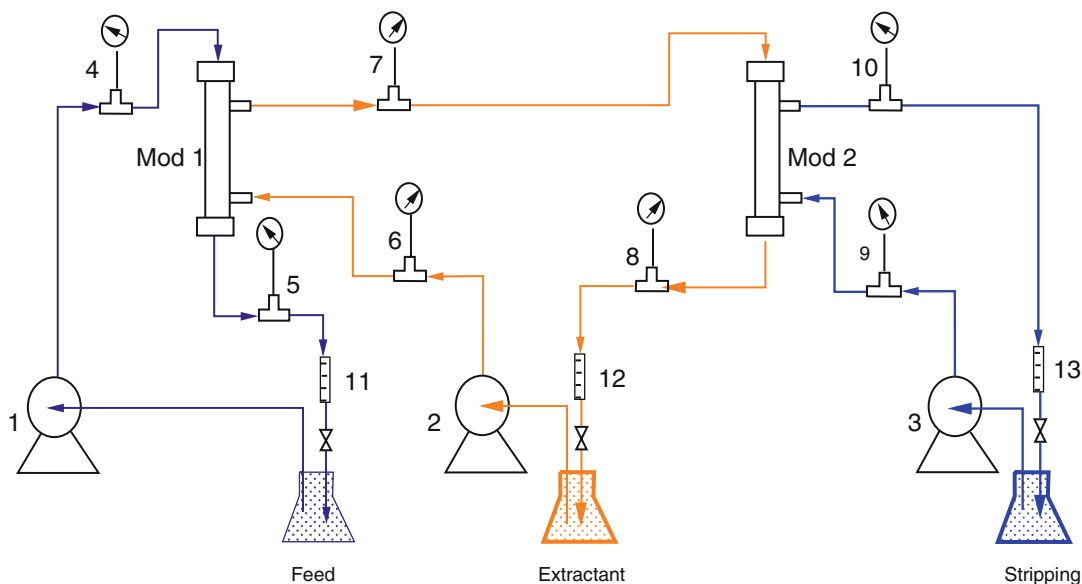
from the liquid/liquid interface immobilized at the pore mouth of the microporous membrane that is not wetted by one of the phases in contact. In this way, dispersion of the liquid phase into the other is prevented. Microfiltration or ultrafiltration membranes are usually used as support to immobilize the interface between the two immiscible phases. In membrane based solvent extraction the membrane has no selective properties, it only serves as support for the immobilization of the interface. Basic information on membrane based solvent extraction are found in Prasad and Sirkar (1992), Reed et al. (1995), Schlosser (2000, 2009).

The solvent can be regenerated by re-extracting the solute in a stripping solution. Figure 2 shows the schematic of a membrane based solvent extraction and stripping using two hollow fiber modules.

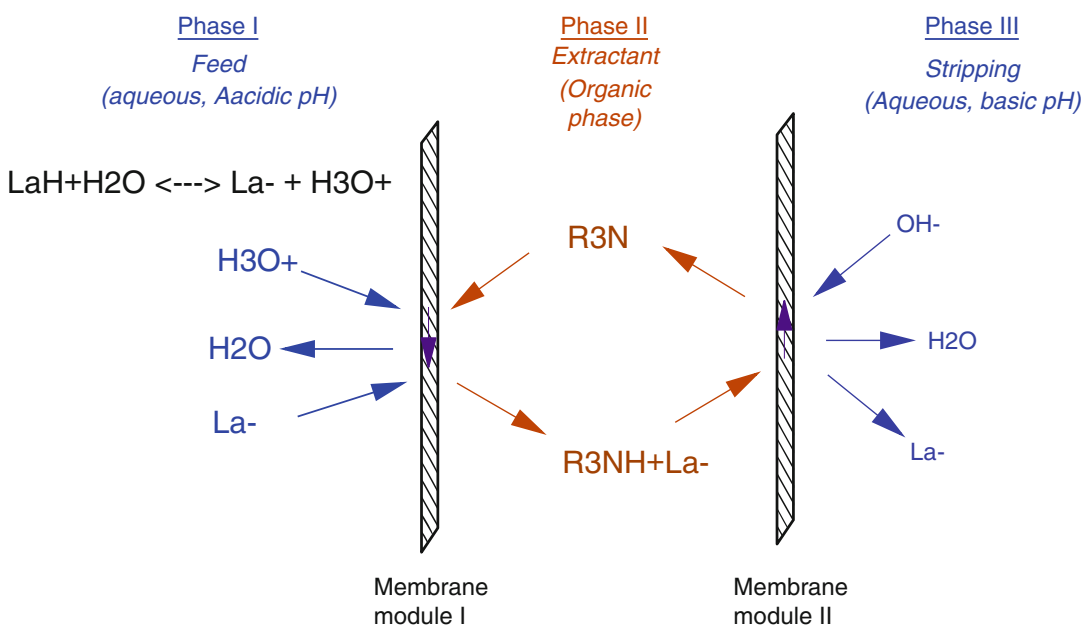
Membrane based solvent extraction is often assisted by a carrier that reacts with the solute at the interface immobilized on the first module and it is released at the interface of the second module. Figure 3 shows the case of extraction of lactic acid by a quaternary amine.

In membrane based solvent extraction mediated by carriers, kinetics of extraction reactions should be taken into account as it can play an important role. The concentration dependence of the distribution coefficient of solutes is another parameter to be taken into the account. The solute distribution coefficient influences the concentration gradient and may result in the concentration dependent overall mass-transfer coefficient.

In the literature, studies using models considering the constant mass-transfer coefficient in MBSE (Viegas et al. 1998), or variable distribution coefficients (Escalante et al. 1998; González-Munoz et al. 2004) are reported. Models taking into account reaction kinetics of formation and decomposition of the extractant-solute complex(es) in extraction and stripping interfaces are also discussed (Juang and Huang 1997; Juang et al. 2000; Kubišova et al. 2004; Schlosser et al. 2001). The contribution of resistance based on reaction kinetics to the overall resistance depends



Membrane Based Solvent Extraction, Fig. 2 Membrane-based solvent extraction in hollow fibre membrane contactors. 1–3 pums, 4–10 pressure gauges, 11–13 flowmeters



Membrane Based Solvent Extraction, Fig. 3 Mechanism separation of lactic acid by membrane-based solvent extraction

on solute and carrier concentrations. It may range between 30 % and 80 %.

Ionic liquids result very promising in the solvent extraction of organics (Han and Armstrong

2007; Pletnev et al. 2008). Ionic liquids (ILs) are composed of organic cations and organic or inorganic anions that remain in liquid state over a wide temperature range, including room temperature.

The majority of works deals with ILs with imidazoliumcations. A new promising group of ILs based on phosphoniumcations (Bradaric et al. 2003).

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Membrane Bioartificial Organs

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Membrane bioartificial organ is a membrane device containing living cells, which is implanted or integrated into a human to replace for short or long term a natural organ. This device is realized as alternative to organ transplantation or as bridge for supporting patients until the organ transplantation. Every year, many patients die while waiting for an organ transplant. Organs such as the liver, kidney, and lungs are often in very high demand by patients with severe illnesses. Historically, the number of available organ donors has been insufficient to meet the needs of every patient. For a traditional organ transplant to succeed, the donor and patient must be a close biological match. Even when a replacement organ is available, the immune system of the recipient may reject the transplant. Membrane bioartificial organs have been designed to solve this problem. Some examples are represented by membrane bioartificial liver for the treatment of acute and chronic liver disease, bioartificial pancreas as alternative approach to exogenous insulin administration in the case of insulin-dependent diabetes mellitus, bioartificial kidney for people with poorly functioning kidneys, and bioartificial lung for the treatment of patients with end-stage lung disease. Membrane capsules containing dopamine-secreting cells are also being explored for the treatment of Parkinson's disease, a progressive brain disorder characterized by a deficiency of the neurotransmitter dopamine. Immunoprotective membrane cell transplants are being investigated to treat other nervous system disorders. Other membrane bioreactors are used for the adoptive cell therapy for the treatment of malignant diseases or viral infections in the expansion of T lymphocytes (Jagur-Grodzinski 2006).

Membrane bioartificial organs involve the design, modification, growth, and maintenance of living tissues embedded in natural or synthetic scaffolds to enable them to perform complex biochemical functions, including adaptive control and the replacement of normal living tissues. In membrane bioartificial organs, cells are compartmentalized by means of semipermeable membranes that permit the transport of nutrients and metabolites to cells and the transport of catabolites and specific metabolic products to the blood (Drioli and De Bartolo 2006). The membrane must avoid the contact between cells and patient's blood to prevent immunological response and consequent rejection. Membranes act also as means for cell oxygenation and in the case of anchorage-dependent cells as substrata for cell attachment and culture. In these systems, cells come into contact with the membrane surface. Therefore, the response of the cell behavior depends on the surface properties of the used membrane (Morelli et al. 2010). For this reason, membranes should be chosen not only on the basis of their separation properties but also on the basis of physicochemical and morphological surface properties. Membrane bioartificial organs are engineered to be used as extracorporeal devices or implantable systems. These devices can be distinguished on the basis of membrane material configuration, molecular weight cutoff or pore size, and cell culture technique. Cells can be compartmentalized in the lumen or shell of hollow fiber membranes (HFMs) or between flat-sheet membranes, in a network of HF membranes, spirally wound module, encapsulated or attached to microcarriers.

The most common membranes used in the membrane bioartificial organs are hydrophilic membranes with molecular weight cutoff ranging from 20,000 to 120,000 daltons, which are chosen on the basis of the molecules that have to provide to the cells and removed from them. The creation of a physiological environment requires the use of membranes with specific physicochemical, morphological, and transport properties on the basis of the targeted tissue or organ (De Bartolo et al. 2012).

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Membrane Biocompatibility

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Synonyms

Biocompatibility of membranes

Membrane biocompatibility is the ability of membrane to perform its intended function without eliciting any host undesirable local or systemic effects. Membrane biocompatibility is a general term that must be subcategorized on the basis of the membrane applications in order to be able to make more narrow definitions. In the case of membranes used in the hemodialyzers, hemofilters, hemodiafilters, and blood oxygenator, the more appropriate term is blood compatibility or hemocompatibility because of the main interactions between membrane and blood. When blood comes into contact with an artificial surface, protein adsorption occurs in the first seconds. Proteins like albumin, immunoglobulin G, fibrinogen, fibronectin, factor XII, and high molecular weight kininogen are adsorbed forming a layer that supports the platelet adherence. The adsorption of thrombin may activate the clotting cascade

(Ulhenbusch et al. 2004). The protein adsorption process is strongly dependent on the physico-chemical (e.g., surface charge, functional groups) and morphological (e.g., porosity, roughness) surface properties of the membranes (De Bartolo et al. 2004). On the other hand, the artificial surface may activate the complement cascade through the membrane-bound complement factors such as C3b and iC3b. After the protein adhesion, platelet changes their morphology, release factors, and aggregate. The adsorbed proteins activate also the coagulation cascade with the fibrin and thrombus formation, which occur within several minutes. The coagulation pathway consists of a series of reactions, each requiring the formation of a surface-bound enzyme complex. In these reactions, inactive precursor proteins are transformed into active protease.

Several studies indicated that platelet activation increases in the positively charged membrane and decreases in the membrane having a microdomain structure in which hydrophilic and hydrophobic groups coexist randomly as molecules. Also, the complement activation, which in the case of biomaterials proceeds via alternative pathway, is mainly noted with cellulose membranes; free hydroxyl groups on the membrane surface are bonded with C3b and further with factor B that promotes the activation. Improvements of biocompatibility of cellulose membrane can be obtained by surface modification devoted to graft, for example, alkyl group to the hydroxyl group.

When membranes are used in bioartificial systems (bioartificial organs and tissues), it is important to consider the cytocompatibility of membrane on which depends the response of the biological components. In bioartificial systems, cells come into contact with the membrane surface. Therefore, their morphological and functional response depends on the surface and transport membrane properties. Physicochemical properties, including surface composition, charge, energy, and morphology, may affect cell adhesion and behavior. In vivo cells are surrounded by the extracellular matrix (ECM) that provides physical architecture and mechanical strength to the tissue.

The native ECM exhibits from macro- to nanoscale patterns of chemistry and topography. For this reason, the cells can respond to various chemically and/or topographically patterned features. When cells are cultured in vitro, they receive very different physical, chemical, and mechanical stimuli from the unfamiliar surrounding environment. Micro- and nanoscale mechanical properties of the membranes are critical because the cells not only adhere to the surface but also pull on the surface substrate and on adjacent cells. The surface chemistry of the membrane affects the adhesion of cells through the ECM protein adsorption and stereospecific chemical interactions. Several approaches have been undertaken to improve the cytocompatibility of membranes by increasing the wettability or by surface modification through grafting of functional groups or immobilization of peptides, and proteins, which interact with the cell receptors (De Bartolo et al. 2005, 2006, Salerno et al. 2009). It is known that the cytocompatibility of the membrane can be increased by modulating its surface free energy and roughness (De Bartolo et al. 2002). It has been shown a significant enhancement of the hepatocyte adhesion and metabolic functions on membrane with high value of surface free energy base parameters.

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Membrane Bioelectrochemical Reactor

► Bioelectrochemical MBR

Membrane Biomaterial

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Membrane biomaterial is any material constituted of membrane that is in contact with biological fluids, organs, tissues, and cells (Williams 2009). Membranes are used as components of medical devices and implants, drug delivery systems, diagnostic assays, and bioreactor and bioseparation processes. They are employed in the replacement therapy for acute and chronic organ failure and in the management of immunological disease as well as in the tissue engineering for the realization of tissue-engineered constructs and defined models supporting investigations on cell function, tissue development, and drug testing. In many clinical therapeutic blood processes are used membrane devices for the removal of endogenous or exogenous toxins from blood (hemodialysis, hemofiltration, hemodiafiltration, plasmapheresis) or for the gas exchange with blood (blood oxygenation) (De Bartolo and Drioli 1998). Membranes of suitable molecular weight

cutoff are used in bioartificial organs (e.g., the pancreas, liver) for compartmentalization of cells and as selective barriers to prevent immune system components from getting into contact with the implant while allowing nutrients and metabolites to permeate freely to and from cells. Membrane-based biomaterials can be realized with different properties on the basis of the functions to be performed. Membranes can be porous or dense, hydrophilic or hydrophobic, natural or synthetic, biodegradable or not biodegradable, and stiff or elastic. However, all membranes properties play an important role in the interactions with cells or biological fluids. Physicochemical properties, morphology, roughness, permeability, and mechanical characteristics affect the biological response and consequentially the performance of the membrane. As a result, the biocompatibility and cytocompatibility of the membrane biomaterial are dependent on its properties related to the application in cells, tissues, organs, and blood. To meet the needs of the biomedical requirements, membranes have to be compatible with biological systems performing their function with an appropriate host response (Ratner et al. 2012). The interactions may involve, for example, platelet aggregation and blood coagulation in the case of blood-contacting devices, immune response, and foreign body reactions when the membrane biomaterials or devices are implanted in the body. The interactions with cells may involve a structural and functional connection or may lead to the cell death and nonviable tissue-engineered constructs.

The most common synthetic membranes used in biomedical applications are made of cellulose acetate (CA), nitrocellulose (CN), and cellulose esters (CE), polysulfone (PS), polyethersulfone (PES), polyacrylonitrile (PAN), polyamide (PA), polyimide (PI), polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyarylethersulfones (PAES), polyvinyl chloride (PVC), ethylene vinyl alcohol (EVAL), polyethyleneimine (PEI), and polymethyl methacrylate (PMMA) (Baker 2004). These membranes are used extracorporeally connected to the patient's body

through blood circulation as, for example, in hemodialysis, hemodiafiltration, blood oxygenation, and bioartificial organs.

In tissue engineering or in implants are used mainly biodegradable membranes that undergo hydrolytic or enzymatic degradation. These membranes are mainly made of polyglycolide or poly(glycolic acid) (PGA), polylactide (PLA), poly(lactic-co-glycolic acid) (PLGA), polycaprolactone (PCL), polycarbonate (PC), polyurethanes (PU), polyphosphazenes (PPHOS), polyamide (PA), chitosan (CHT), hyaluronic acid (HA), collagen, and poly(p-dioxanone) (PDO). Biodegradable membrane biomaterials can be implanted in situ into the body. An example is the commercial collagen resorbable membrane from highly purified type I collagen that is used for repairing tears and wound healing. Specifically, membrane biomaterials that are biodegradable provide the significant advantage of being able to be broken down and removed after they have served their function (De Bartolo and Bader 2013).

Responsive membranes are used in the area of cell sheet engineering for the in vitro tissue reconstruction. These membranes allow the adhesion and proliferation of cells at a temperature above the lower critical solution temperature of the grafted polymer (a state where in the surface is hydrophobic) and the detachment of cells when the temperature is lowered below the lower critical solution, because of spontaneous hydration of the grafted polymer chains.

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Membrane Bioreactor

- [Aerobic Membrane Bioreactor](#)
- [Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study](#)

Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study

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Synonyms

[Decentralized wastewater treatment system](#); [Membrane bioreactor](#); [Permeate](#); [Water reuse](#)

Nowadays, decentralized wastewater treatment system (WWTS) becomes interested treatment technology in many countries. To catch up the wastewater treatment requirement, there are many decentralized biological wastewater treatment technologies used such as conventional activated sludge process, trickling filter, oxidation ditch, rotating biological contactor, etc. Besides, these technologies seem to be appropriate only to the available construction area (Günder and Krauth 1999). The MBR technologies have evolved drastically in the recent period, and the technology proves many advantages in considerably reducing the foot-print requirement to treat a given flow, increasing the volumetric loading rate, augmenting the effluent quality (Lobos et al. 2007; Thanh et al. 2008), and trimming down the chemical requirements for disinfection.

The initial development of MBR technology began in the late 1960s, which is the platform of

Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study,

Fig. 1 Small and limited parking lot at Caravelle Hotel



rapid growth in the early 1990s (Stephenson et al. 2000). Presently, MBR application becomes popular around the world owing to many striking advantages. Some hotels are among pioneers of MBR technology application in WWTS.

A case study of a renowned hotel in Ho Chi Min City is here reported. Total wastewater generated mainly from hotel operation with capacity of 350 m³/day includes sources from toilets, lavaboes, kitchens, food courts, and restaurants. Before 2010, there was only one three-chamber septic tank for treating entire wastewater in the hotel, which cannot comply with the new environmental regulation. The regulation is changing day by day and becomes stricter with treated wastewater discharging to the environment – QCVN 14:2008/BTNMT. Consequently, it is really essential to have upgraded WWTS coupling with the existing septic tank in the hotel so as to improve the treated water quality not only to meet the new current regulation but also to reuse treated water for many purposes. Nevertheless, modification plan of WWTS is not included in the initial construction plan of the hotel managers which leads to limited construction space for the new system. Many implemented surveys show that only parking lot at the basement can be the only place for new WWTS. After weighing the pros and cons of many proposed technologies, the MBR technology seems to be

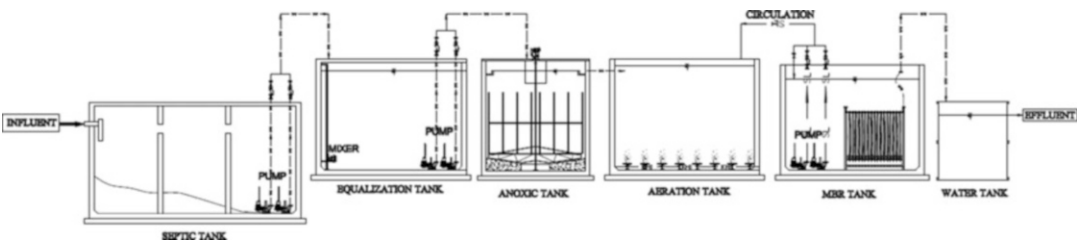
the proper choice in this case instead of the conventional activated sludge process which requires large area for sedimentation and disinfection tank. Because of 70 % of space saving, membrane system becomes smart and appropriate choice for such small parking lot at basement of the hotel (Fig. 1).

Membrane Bioreactor Technology: Decentralized WWTS for Caravelle Hotel

Wastewater generated from Caravelle Hotel is gathered and contained in the existing septic tank for pretreatment before being pumped into equalization tank later using two submersible pumps. The equalization tank is responsible for regulating flow rate as well as pollutant concentrations in wastewater to avoid overloading for later unit processes. Wastewater is then pumped into anoxic tank and aeration tank (called A/O process) in order to achieve degradation of organic matters, nitrification, and denitrification process. Compressed air is supplied continuously to aeration tank using two air blowers and diffuser system to maintain the stable growth and development of microorganism. Membrane modules were inserted into the second chamber of the aeration tank. With the pore size of 0.4 µm hollow fiber membrane, most of the sludge particles and

Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study, Table 1 Membrane characteristics

No	Image	Parameters	Unit	Value
1		Manufacturer	–	mitsubishi – Japan
2		Branch/model	–	SADF0690
3		Surface area	m ²	6
4		Number of elements	Element	60
5		Pore size	µm	0.4
6		Fiber diameter	mm	2
7		Dimension (D × W × H)	mm	30 × 620 × 1015
8		Temperature	°C	5–40 °C
9		Range of pH	–	1–11
10		Design capacity	m ³ /(element.day)	1.2–4.8
11		Air flow rate	m ³ /(element.day)	0.05–0.07



Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study, Fig. 2 Technical diagram of wastewater treatment system at Caravelle Hotel

microorganisms such as *E. coli* and coliforms are retained inside the aeration tank and eliminated out off the membrane permeate. The membrane characteristics are summarized in Table 1 and the process diagram of WWTS is demonstrated in Fig. 2 (Table 2).

Table 3 shows that all required parameters such as BOD, ammonia nitrogen, nitrate nitrogen, and total coliforms comply with Viet Nam national technical regulation – level A, QCVN 14:2008/ BTNMT after long-term operation. Especially, turbidity removal reaches maximum value of 98–100 %. The superior results show the excellent application of MBR technology in Caravelle Hotel.

Another special benefit of MBR technology which cannot help to be mentioned is reusing ability of treated wastewater after MBR treatment for many purposes such as toilet flushing, floor washing, watering, or cooling water for central air conditioning system in the hotel. Notwithstanding, tea like color appearing in treated

Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study, Table 2 Operating conditions of the MBR system

Operating conditions	Value
Flux, L/(m ² h)	10
Trans-membrane pressure (TMP), kPa	20
MLSS, g/L	3.5–4.0
SRT, d	∞
HRT, h	0.6–2.0
F/M, d ^{−1}	0.15–0.30
OLR, kgCOD/m ³ .d	0.2–0.5
Recirculation ratio (Q _r /Q)	2
Air flow rate, Nm ³ /h per module	20–27
Operational temperature, °C	25–35
pH	6.8–7.5
Cleaning in-line frequency	7 days ^a
Cleaning duration	30 min

^aUsing NaOCl solution for cleaning in-line

water (after MBR treatment) failed observational regulation for reusing purpose even good quality. Thus, the ion exchange columns followed by ozone system are installed to remove color in

Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study, Table 3 MBR performance (Data from 30 samples during operation)

Parameters	MBR system		QCVN 14:2008 (level A)	Japan reuse standards for toilet flushing and irrigation
	Removal efficiency (%)	Membrane permeate ^a		
pH	–	5.0–6.5	5–9	5.8–8.6
Turbidity, NTU	98–100	0–1	–	<2
Color, Pt-Co	70–97	20–50	–	–
COD, mg/L	78–94	15–45	–	–
BOD, mg/L	87–92	8–16	30	20
NH ₃ -N, mg/L	–	–	5	–
TKN, mg/L	42–65	15–30	–	–
NO ₃ -N, mg/L	–	8–30	30	–
Total coliforms, MPN/100 mL	8–9 log	90–1200	3000	–

^aRemark: without chlorination applied

MBR permeate. After additional treatment step, treated wastewater can be reused inside the hotel as per the abovementioned activities. Total amount of reusable water can be estimated approximately of 180 cubic meter per day compared to total wastewater generated with capacity of 350 cubic meter per day.

By and large, MBR technology becomes potential and attractive application not only in Viet Nam but also all over the world in the near future. Notwithstanding, there are still issues in MBR system operation, especially specific problems relating to MBR such as membrane fouling which need further researches to be perfect. Despite some disadvantages, MBR technology will be always considered as an optimal treatment solution because of high treated effluent, space saving, automatic operation, and easy maintenance; especially for limited foot-print area like Caravelle Hotel. The MBR technology gradually becomes dominant technology in the urban cities of Viet Nam.

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Membrane Bioreactor Using Extremophiles

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Membrane bioreactors are apparatuses, like stirred tank reactors, traditional fermentation vessels, or tubular reactors, that are implemented with additional separation devices based on membrane modules to permit the medium exchange at request during bioprocessing. Membrane bioreactors have been exploited in the cultivation of demanding organisms, such as extremophiles, or

in order to meet productivity target in pilot scale or even industrial-scale biotechnological production processes. Extremophiles are peculiar microorganisms that can grow and thrive in extreme environments, which were formerly considered too hostile to support life. They are structurally adapted at the molecular level to withstand at least one of the following harsh conditions: very high (hyperthermophiles) or low temperature, high or low pH, high salinity (halophiles), high metal/organic compound concentrations, high pressure, and low oxygen tension. A few of them proved resistant to multiple stress conditions. The biocatalysts, called extremozymes, produced by these microorganisms, are proteins adapted to function under these extreme conditions. Due to their outstanding stability, extremozymes have great potential for application in various biotechnological processes. Notwithstanding this natural resource and the remarkable opportunities that these uncommon organisms present for biotechnological applications, only few have been commercially exploited because of the difficulties encountered in attempting their cultivation. Hence, special equipment and custom-tailored processes have been developed and are currently under evaluation for the improvement of fermentation productivity. Specific fermentation apparatuses have been employed in the extremophilic biomass and related product production with sound results at a laboratory scale. The pioneering dialysis bioreactor was designed by the biotechnology group at the Technical University of Harburg-Hamburg (Krahe et al. 1996), developed and constructed by bioengineering at 1 and 5 L scale. The dialysis fermenter was used in the cultivation of the hyperthermophile *Pyrococcus furiosus*, the thermoacidophile *Sulfolobus shibatae*, and the halophile *Marinococcus* M52 resulting in high cell yields up to 40-fold with respect to the corresponding batch experiments. The main idea was to assure the removal of (unknown) toxic compound while sustaining growth through appropriate nutrient feeding. On the lab scale, this was achieved through a massive external dialyses, generating wastewater but assuring an efficient increase in biomass final density. A similar approach, based on

Membrane Bioreactor Using Extremophiles,

Fig. 1 Microfiltration modules fixed to the baffles of a 15 L fermenter



microfiltration (pressure-driven exchange rate) in place of dialysis, was developed by Prof. De Rosa's group (Schiraldi et al. 1999, 2001). The specific microfiltration modules (Fig. 1), tailor made, biocompatible, and resistant to the harsh cultivation condition, were assembled at the Second University of Naples; also the bioreactor vessel (Sartorius Stedim, BBI, Germany) was modified with module insertion next to the baffles and investigated for improving efficiency of extremophilic biomasses and enzyme production. In spite of the difficulties in cultivating hyperthermophiles (70–80 °C, pH 3.5), adopting a specifically developed nutrient-split feeding strategy, in 300 h fermentation, more than 30-fold biomass dry weight increase was achieved for *Sulfolobus solfataricus*, and the activity of the constitutive enzyme alcohol dehydrogenase (ADH) was not affected by cell density. Modifying the cultivation condition and the medium exchange rate, the MF fermentation strategy proved effective in the production of compatible solutes from *Marinococcus* M52 (Schiraldi et al. 2006). Membrane bioreactors proved effective in enhancing final cell densities in hyperthermophile, acidophile, and halophile cultivations. However, a recent review of Alain and Querellou (2009) suggests that the main hindrance to extremophile cultivation is likely due to the prevailing lack of knowledge on targeted species. These scientists focus on the limiting factors surrounding cultivation also discussing potential issues including the loss of

microbial cell-cell communication following species isolation and finally suggesting future research directions.

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- Membrane bioreactors is the general term indicating a membrane reactor using a catalyst of biological origin. Similar terms commonly used include “biochemical membrane reactors,” “biological membrane reactors,” “membrane fermentors,” “biocatalytic membrane reactors,” and “enzyme membrane reactors.” Table 1 summarizes the most common biocatalysts used as well as the role played by the membrane (Drioli and Giorno 2010; Mazzei et al. 2013). Most membrane operations have been used as separation process in membrane bioreactors, including pressure-driven membrane processes, membrane-based solvent extraction, membrane contactors, electrodialysis, and forward osmosis.

In general, the membrane can work simply as a separation unit, or it can function also as a support for the biocatalyst (in this case biohybrid systems are obtained and the reactor is more appropriately termed “biocatalytic membrane reactor,” meaning that the membrane has catalytic properties). In the first case, the reaction occurs in a tank connected to a membrane module where the separation occurs. The reaction and transport rate can be governed independently. The membrane has an indirect effect on the reaction by controlling the mass transport in and out of the reaction environment, i.e., removing products, adding reagents, and retaining the catalyst in the reaction bulk phase. The membrane module can be placed externally to the tank (side-stream configuration) or it can be immersed into the tank (submerged configuration) (Fig. 1; Judd, 2010).

In the biocatalytic membrane reactor, the reaction occurs at the membrane level. The transport rate may influence the reaction performance. The membrane has both a direct effect on the reaction and governs the mass transport through the reaction environment.

Figure 2 illustrates the general classification of various biochemical membrane reactors. Here, schematics represent the external or side-stream configuration, in which case the membrane modules are outside the bioreactor and solution is recirculated through a membrane separation loop (Drioli and Giorno 1999, 2000; Mazzei 2010). However, also submerged (or immersed) membrane configuration can be used.

Membrane Bioreactor Using Ultrafiltration Membranes

► Ultrafiltration Membrane Bioreactor

Membrane Bioreactors

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Synonyms

Biocatalytic membrane reactors; Biochemical membrane reactors; Biological membrane reactors; Enzyme membrane reactors; Membrane fermentors

Membrane Bioreactors, Table 1 Biocatalysts used in biological membrane reactors

Biocatalyst	Status	Common membrane role	Reaction components properties
Enzymes	Compartmentalized	Enzyme recycle, product separation, and/or reagent supply	Enzymes need cofactors, substrates are large polymers, reaction mixture is very viscous
	Immobilized on membrane surface	Support for the catalyst	The size of the substrate is too big to enter the membrane matrix, products can pass through the membrane
	Immobilized within the membrane matrix	Support for the catalyst, reagent supply, product separation	The size of the substrate and products is suitable to be transported through the membrane
Bacteria cells	Compartmentalized	Cell recycle, products and/or purified components separation, and/or reagent supply	Cells operate the transformation of interest during the growing phase of the fermentation
	Immobilized	Support for the catalyst, reagent supply, product separation	Cells can operate the transformation of interest during a phase different than the growing one
Fungi	Compartmentalized and/or attached on the membrane surface	Biocatalyst recycle, components separation	Biocatalyst grows in the bulk phase and/or it needs to attach on a surface to form a biofilm
Yeast			
Virus			
Algae/microalgae		Biocatalyst growth	
Mammalian cells	Compartmentalized	Cell recycle, metabolites supply, catabolites removal	Cells, such as red cell blood, lymphocytes, leucocytes, need to be maintained alive in bulk phase
	Attached	Support for cell growth, metabolites supply, catabolites removal	Cells anchorage dependent, such as hepatocytes, neurons, epithelia, need to adhere to surface for the differentiation and biotransformation

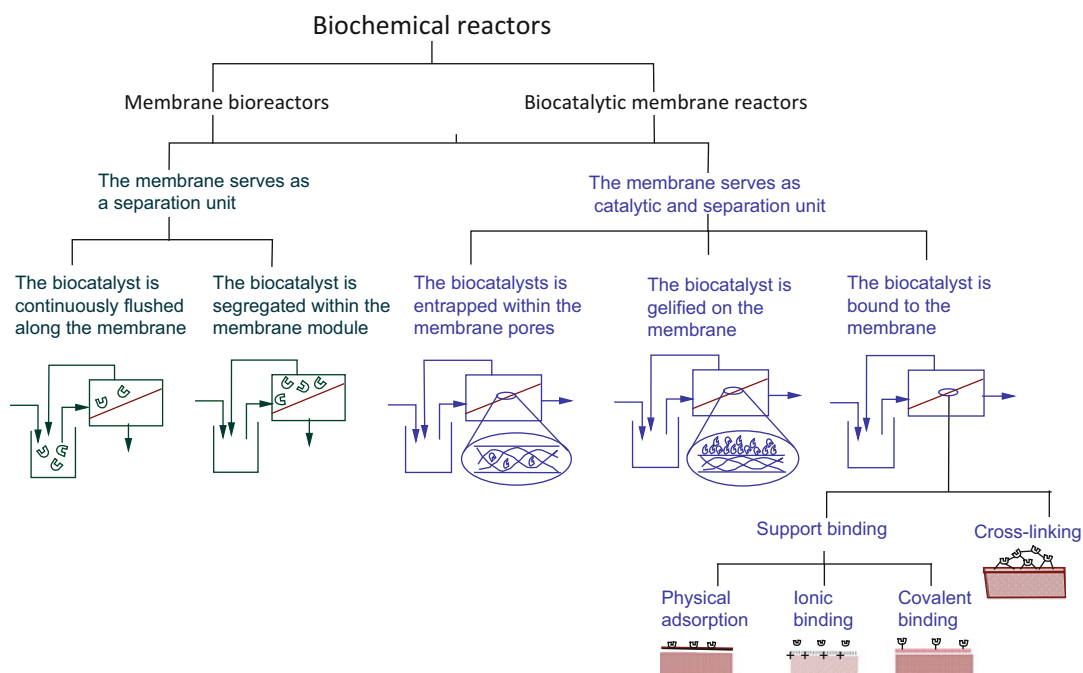
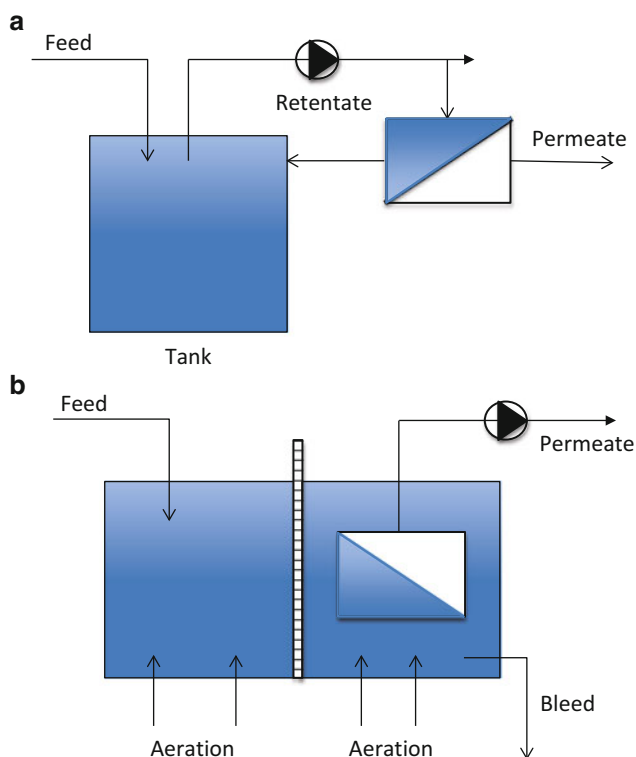
Membrane bioreactors have several intrinsic advantages, including small footprint, continuous operation, biocatalyst reuse, selective supply of substrate, selective removal of the product (thus limiting product inhibition phenomena in addition to maximizing substrate conversion by shifting the reaction equilibrium to the right on the basis of the Le Chatelier principle), and possibility to carry out simultaneously reaction and separation.

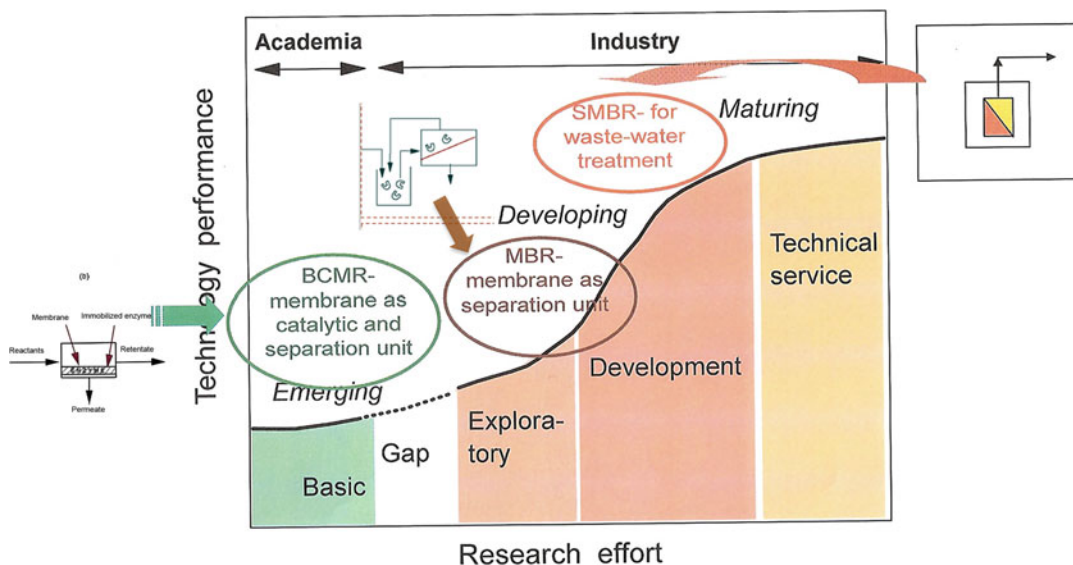
Among the various types of biochemical membrane reactors, the submerged bioreactors are the most used on a large industrial scale. Their concept was conceived in the late 1980s/early 1990s by independent teams in Japan and Canada. They are mostly applied for waste water treatment, even though some investigation for bioreaction is also available. Microorganisms (including bacteria, yeast, fungi, algae) are mainly used as biocatalysts. They are the most recent type of bioreactor conceived; nevertheless they are the

most mature process among the biochemical membrane bioreactors (Fig. 3). Figure 3 illustrates the behavior of a technology performance as a function of research effort and the related location of most common biochemical membrane reactors. It can be seen that significant research efforts have been invested in this technology that rapidly advanced it to a mature stage (Fig. 3).

They are recognized by the directive of the European Commission “The Integrated Pollution Prevention and Control (IPPC) Directive (1996)” among the best available technologies (BAT) for waste water treatment

The external (side stream) membrane bioreactor, using the membrane as a separation unit, is applied in many bioprocessing, in particular in food, biotechnology, pharmaceutical, and biomedical fields. Nowadays, their investigation in the area of biorefining is attracting much attention. Both microorganisms and enzymes are used

Membrane Bioreactors,**Fig. 1** Membrane configuration module (a) Side-stream and (b) submerged configuration**Membrane Bioreactors, Fig. 2** Schematic classification of biochemical membrane reactors (the side stream configuration of the module is reported, but submerged membrane can also be used)



Membrane Bioreactors, Fig. 3 Development stage of various biochemical membrane reactors. (Drioli and Giorno 2010)

as biocatalysts. This type of bioreactor is at a developing stage approaching the mature service stage (Fig. 3).

The biocatalytic membrane reactors, using biocatalyst-loaded membranes, are mainly used as side-stream configuration and are mostly applied in pharmaceutical, biotechnology, and food production. Some examples of submerged biocatalytic membranes have been investigated for water decontamination, biodiesel production, and control of fouling. Even though some bacteria in vegetative stage have been immobilized in membranes, enzymes are the widely used biocatalysts in this type of bioreactor.

As illustrated in Fig. 2, the enzyme can be loaded on the membrane surface or within the porous matrix. It can be entrapped within the porous matrix during the membrane formation by phase inversion promoted by non-solvent-induced phase separation (NIP), or it can be entrapped by cross-flow filtration in already formed membranes. The enzyme can be mechanically entrapped (on the basis of the higher molecular size compared to the pore size of the membrane matrix), physically gelled on the surface of porous membrane (during ultrafiltration the enzyme is retained on the membrane surface

while the solvent is permeated through the membrane; the enzyme is concentrated at the interface up to the precipitation value, forming a gel cake layer of enzyme), or can be chemically bound to the membrane surface and/or porous matrix. Chemical bond includes physical adsorption, ionic binding, covalent bond, and cross-linking.

Despite the large variety of enzymes immobilized in membranes, their investigation for numerous bioconversions, and the great potential they offer for a clean, safe, intensified, and sustainable production, their development is still at an emerging stage (Fig. 3) with research effort limited on a lab scale. The need for highly selective processes able to reduce wastes and by-products may help to change the trend.

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Membrane Bioreactors for Cell Growth

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Membrane bioreactors composed of semipermeable membranes and bioreactors are very attractive for the culture of animal, plant, and microbial cells. For mammalian cell cultures, membrane bioreactors are mainly used to produce biochemicals such as vaccines, interferons, hormones, growth factors, viruses, and monoclonal antibodies and to act as artificial organs. More recently, membrane bioreactors found applications in the area of regenerative medicine for developing functional tissues from cells in combination with a suitable matrix to support and accelerate regenerative healing. In these devices, usually cells are immobilized in a compartment separate from the feed medium containing nutrients that diffuse through the membrane to the cell compartment. Membrane with suitable MWCO allows the retention of cells and the separation of cell products from the feeding stream. Multiple functions are performed by membrane in the bioreactor: (i) compartmentalization of cells, (ii) the selective transport of nutrients and metabolites to

the cells and the removal of catabolites and cell products, (iii) wide surface for adhesion of anchorage-dependent cells, and (iv) protection of cells from shear stress. The efficiency of the overall system depends on the cells (viability, functions, density), membranes (configuration, structure, size, morphology, pore size distribution, physicochemical and mechanical properties), and hydrodynamic parameters (flow rate, transmembrane pressure, residence time, shear stress, etc.). A critical point in the design of an efficient membrane bioreactor for cell growth is the overall transmembrane mass flux of metabolites, catabolites, cell regulatory, and related soluble factors that need to be considered. Molecules contained in the culture medium, which are fed and produced by cells, are comprised on a wide range of molecular sizes (from small electrolytes to large proteins) and physicochemical properties (hydrophilic, hydrophobic molecules). The transport of low MW nutrients and metabolites is assumed to occur by diffusion, whereas convection phenomena are supposed to regulate the mass transfer of macromolecular species and proteins (Giorno et al. 2011). Surface properties of membranes need to be also considered in the design of a membrane bioreactor for the culture and expansion of adherent cells that are in tight contact with the membrane surface. Membranes should have surface characteristics in terms of morphology and physicochemical and mechanical properties that favor the adhesion process and the integration of cells. Membrane bioreactors have been investigated for the culture of lymphocytes, liver cells, embryonic stem cells, progenitor cells, and stem cells. These devices have been used in replacement therapy for acute and chronic organ failure and in the management of immunological disease as well as in tissue engineering for the realization of tissue-engineered constructs and defined models supporting investigations on cell function, tissue development, and drug testing. Different configurations of membrane bioreactor have been explored for the culture and growth of mammalian cells. Primary cells, immortalized cells, and stem cells can be cultured (a) on flat-sheet membranes, (b) in the lumen or shell of hollow

fiber membranes in suspension or attached to the membrane surface, (c) in a network of hollow fiber membranes, (d) in a spirally wound membrane device, (e) in multibore fibers, and (f) in gas-permeable membrane bioreactor. Flat membrane bioreactor is a simple device that has been developed for the small-scale culture of cells (e.g., neurons, hepatocytes) as tool for drug screening and toxicological studies (De Bartolo et al. 2006a). In this device a microporous flat-sheet membrane separates the medium compartment from the cells that are adhered on the membrane. Advanced bioreactors use additionally gas-permeable membranes (e.g., fluorocarbon membranes), which are permeable to oxygen, carbon dioxide, and water vapor, in order to improve the oxygenation of cells. In this device cells receive oxygen directly from the bottom membrane sheet where they are seeded and indirectly from the microporous membrane in contact with the medium overlaying the cells (De Bartolo et al. 2006b). Hollow fiber membrane bioreactors are the most used bioreactors for high cell density culture. In these devices cells usually are cultured in the shell of a bundle of hollow fiber membranes parallel-assembled, and the medium flows in the lumen (De Bartolo et al. 2007b). Alternatively cells can be cultured inside the lumen of hollow fiber and the medium flows in the shell (Demetriou et al. 1986). In both cases the medium and cell compartments communicate through the pores of the fiber wall. Advanced designs of bioreactors using a network of hollow fiber membranes with different properties have been developed for the culture of cells in order to improve the mass transfer (Gerlach et al. 1994). Spirally wound bioreactor has been proposed for the culture of hepatocytes and other mammalian cells. This bioreactor consists of spiral-wound membranes, and some devices include also a layer of polypropylene hollow fiber membranes for cell oxygenation (Flendrig et al. 1997). Bioreactors using multibore capillaries have been developed in the last years for the culture of human hepatocytes (De Bartolo et al. 2007a). This device is composed of multibore membranes of modified poly(ethersulfone) constituted of

seven compartments represented by seven capillaries arranged in one single fiber. The seven compartments communicate through a porous foamy support structure that is located in between the capillaries. In this bioreactor human hepatocytes have been cultured inside the lumen of the multibore fibers and lumen in the shell compartment. In the last years membrane bioreactors have been developed for the expansion and transdifferentiation of stem cells to be used in cell therapy and tissue engineering applications (Salerno et al. 2013).

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Membrane Bioreactors for Treatment of Tannery Effluents

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Synonyms

Industrial/tannery wastewater treatment using
membrane bioreactors

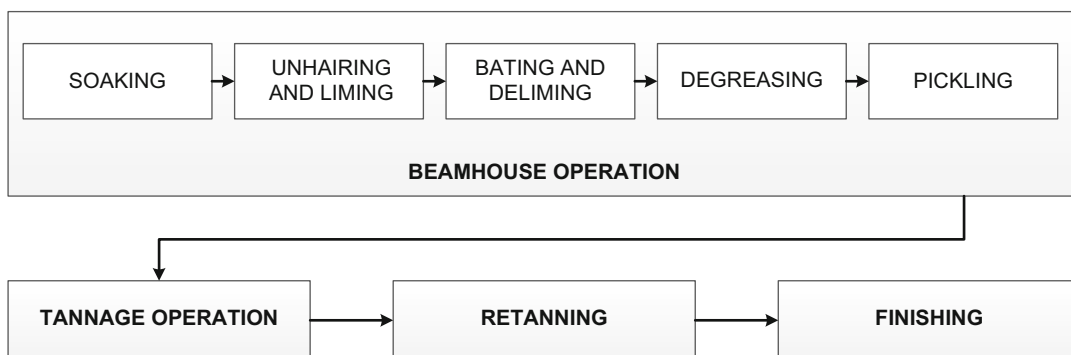
Introduction

The tanning process aims to treat animal raw skins to produce leather, which is more durable and less susceptible to decomposition. The whole process includes several procedures as shown in Fig. 1: beamhouse operation, tanyard processes, retanning, and finishing (Tunay et al. 1995; Cooman et al. 2003; Lofrano et al. 2013). In general, tanning can be performed with either vegetable or mineral methods. However, the mineral method (e.g., chrome tanning) is faster than vegetable tanning (less than a day for this part of the process) and produces a stretchable leather which is excellent for use in handbags and garments.

The wastewater amount generated from tannery industry is in a wide range (10–100 m³ per

ton hide) dependent on the raw material, the finishing product, and the production processes (Tunay et al. 1995). Characteristics of tannery wastewater are summarized as follows: pH 6–11; chemical oxygen demand (COD), 2100–11,000 mg/L; biochemical oxygen demand (BOD₅), 100–2900 mg/L; total suspended solids (TSS), 500–2900 mg/L; total dissolved solids (TDS), 6800–37,000 mg/L; alkalinity, 600–1000 mg/L; sulfide, 30–900 mg/L; ammonia, 30–350 mg/L; and chromium, 10–260 mg/L (Lofrano et al. 2013). In general, tannery wastewaters include high organic concentration, high salt content, and various inhibitory compounds, which must be properly treated.

Membrane bioreactor (MBR) processes, which use membrane filtration units to replace the secondary clarifier, offer several prominent advantages over the conventional activated sludge processes, such as improved effluent quality, higher volumetric organic load, reduced footprint, and less sludge production (Wang et al. 2008; Judd 2011). MBR can be operated under longer sludge retention time (SRT), which facilitates the growth of microbes that have long generation time. This will enhance the pollutant removal efficiency due to the presence of those microbes that may be absent in conventional activated sludge (CAS) processes. For instance, the slow-growing nitrifying bacteria can be enriched in MBRs, leading to the improved nitrification efficiency (Lin et al. 2012). The high biomass concentration maintained in MBRs also contributes to the enhanced degradation of recalcitrant organic



Membrane Bioreactors for Treatment of Tannery Effluents, Fig. 1 Unit processes in leather production

matters since the dominant bacteria and microbial community diversity might be increased compared to CAS systems (Ma et al. 2013). Therefore, the use of MBR for tannery wastewater treatment can achieve relatively better effluent quality compared to CAS systems. The COD and ammonia removal efficiencies are usually more than 90 % in MBRs with proper design and operation (Lin et al. 2012). In terms of heavy metal (e.g., chromium) treatment, the combination of MBR process and low-cost additives can effectively remove chromium (Malamis et al. 2009).

As for the design of MBR for tannery wastewater treatment, both submerged and external MBR configuration can be adopted. Membrane modules including hollow fiber, tubular, and flat sheet modules can be used. In general, hydraulic retention time (HRT) varies from 0.33 to 4.16 days, while solid retention time (SRT) is usually in the range of 5–150 day (Lin et al. 2012). The combination of anaerobic pretreatment (e.g., upflow anaerobic sludge blanket) with MBR is recommended.

Cross-References

- [Membrane Biotechnology](#)
- [Ultrafiltration Membrane Bioreactor](#)

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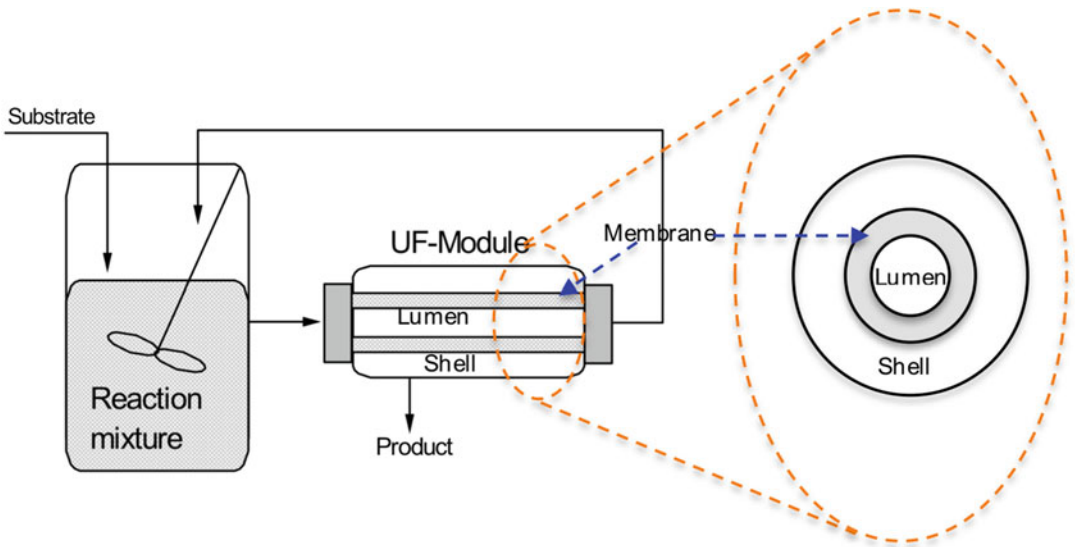
Membrane Bioreactors with Biocatalyst Segregated in the Membrane Module

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In these reactors, enzymes or cells are not linked but only confined in a defined region of membrane module space. The segregation of the biocatalyst is achieved by means of membranes with a suitable molecular weight cutoff. In this way, enzymes and bacterial cells are not lost in the effluent stream, and low-molecular weight products and inhibitors can be removed through the membrane (Fig. 1). The development of hollow fibers with diameters down to about 100 μm makes possible tube-and-shell reactors with a high surface-to-volume ratio.

Membrane can segregate enzymes or cells either within the hollow fiber lumen or within the shell surrounding the outer surface of the fibers. Figure 2 shows the case where the biocatalyst is segregated within the lumen of capillary membrane, which separates the product of the bioconversion.

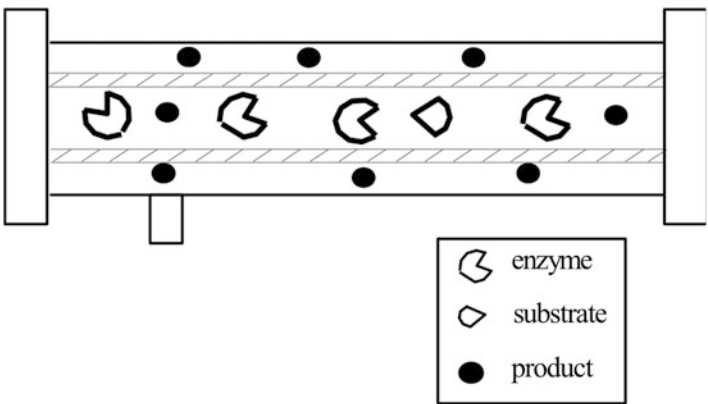
The case where the biocatalysts are present within the porous membrane support are more appropriately said “biocatalysts entrapped” rather than “segregated,” to account for the more reduced space around the biocatalyst. There is growing interest in therapeutic applications of compartmentalized cells or microsomes



Membrane Bioreactors with Biocatalyst Segregated in the Membrane Module, Fig. 1 Schematic of a membrane module with capillary membrane module

Membrane Bioreactors with Biocatalyst Segregated in the Membrane Module,

Fig. 2 Membrane module with biocatalyst segregated within the lumen of capillary membrane



Membrane Bioreactors with Biocatalyst Segregated in the Membrane Module, Table 1 Most common application of membrane bioreactors with segregated biocatalyst

Bioconversion (biocatalyst)	Membrane bioreactor	Application
Insulin secretion (Langerhans islets)	Polyamide capillary membrane (pore size: 10–100 nm)	Bioartificial pancreas
Liver metabolism (hepatocytes)	Polysulfone capillary membrane (pore size: 10–100 nm)	Bioartificial liver
Cellular metabolism (cancerogenic cells)	Polysulfone capillary membrane (pore size: 0.1–1 μm)	Study of cancerogenic cell growth/differentiation

functioning as a bioartificial pancreas or extracorporeal detoxification device (Goosen et al. 1985; Takabakate et al. 1991). Evaluation of stability and catalytic properties of the immobilized system must take into account possible pH differences between the inner core of the fiber, where the reaction takes place, and the bulk of the feed solution.

The most common application of membrane bioreactor with cells segregated at the level of the membrane module (lumen or shell) is summarized in Table 1.

Membrane processes play a key role in modern therapy for treating acute and chronic organ failure and in the management of immunologic diseases. In fact, membrane devices are employed in most extracorporeal blood purification methods, and the next generation of artificial organs and tissue engineering therapies is likely to be grounded on membrane technology. Intracorporeal uses of membrane devices include contact lens, biosensors, drug delivery systems, and artificial grafts.

The use of membrane bioreactors in the development of new artificial organs is attracting today significant attention. Over 20 million patients are sustained by functional organ replacement. Most of recent research activity has been focused on organ replacement and extracorporeal treatment. Two main strategies are followed: (i) the use of membrane as toxins separator and (ii) the use of cells combined with membrane to remove toxins and supply metabolic organ functions. Membrane bioartificial pancreas using isolated islets of Langerhans segregated by membranes represent an alternative approach to the transplantation of the whole pancreas in patients with insulin-dependent diabetes. Various investigations are directed to protect cells from immunorejection, to maintain the cell viability and functions, to reduce diffusion resistance of nutrients and metabolites, and to study the kinetics of transformation of glucose into insulin.

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Membrane Bioreactors with Membrane Used as a Separation Unit

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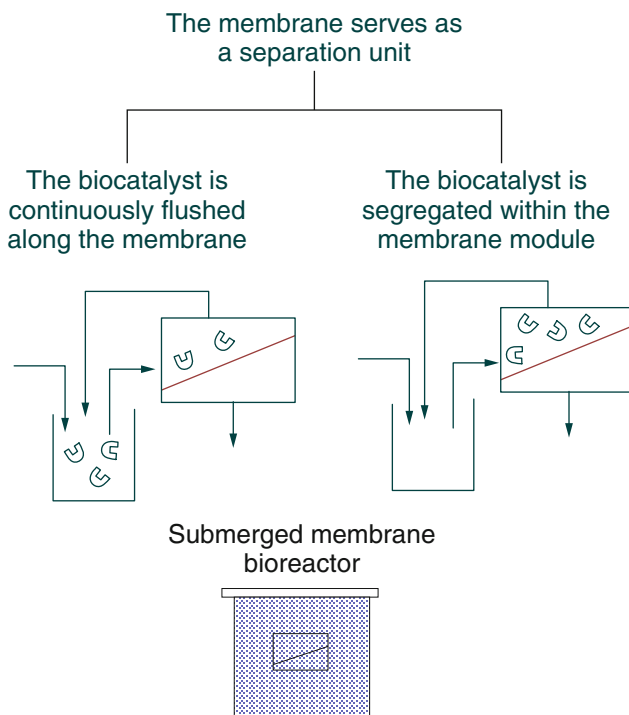
This type of membrane reactor is based on the combination of a continuously stirred tank reactor (CSTR) with a membrane separation process (Fig. 1). The membrane simply acts as a separation unit and does not take part directly to the reaction. The reactor works as a CSTR, but the product passes through the membrane unit where the enzyme is retained and recycled back into the reactor or remains confined in the membrane module.

An appropriate membrane separation is used to keep larger components in the reaction vessel (i.e., enzyme and macromolecular substrates) and remove low-molecular-weight molecules (i.e., product, inhibitor). The biocatalyst is immobilized by the fact that it is compartmentalized by the membrane in the reaction vessel. This allows continuous processing with the biocatalyst suspended in a homogeneous solution. Direct contact between the substrate and biocatalyst limits diffusional resistance.

The most common separation process used in this kind of setup is ultrafiltration (Table 1).

Membrane Bioreactors with Membrane Used as a Separation Unit,

Fig. 1 Membrane bioreactors with inert membrane serving as a separation unit



Dead-end and continuous stirred ultrafiltration cells with flat membranes have been widely used; furthermore, cross-flow ultrafiltration through tubular membrane modules has been investigated.

Concentration polarization phenomena severely affect the performance of reactors where the membrane is used only as a separation media, and then it is necessary to control the polarization layer on the membrane-pressurized side by means of reactor fluid dynamics or appropriate design. Fluid dynamic conditions in some of these reactors make them especially suitable for enzymatic systems for which a homogeneous catalyst distribution is particularly important, such as cofactor-requiring mono- and multienzyme systems.

Enzyme activity is usually not constant with time. Physical chemical changes in enzyme structure, thermal denaturation, and microbial contamination cause enzyme activity to continuously decrease with time. When enzymes or cells are compartmentalized in UF cells, biocatalyst losses can even occur due to the wrong choice of chemical properties and morphology of the membrane.

It is conventional to measure the enzyme stability in terms of its half-life time ($t_{1/2}$); that is the time at which enzyme activity is reduced to half its initial value. It can be calculated from the following equations:

$$t_{1/2} = \frac{0.693}{K_d} \quad (1)$$

$$K_d = \frac{2.303}{\vartheta} \log \frac{A_{E_0}}{A_{E_\vartheta}} \quad (2)$$

K_d is the enzyme deactivation constant; ϑ is the operation time; A_{E_0} is the initial enzyme activity or product mass per unit time and reaction volume; A_{E_ϑ} is the enzyme activity at time ϑ .

Since biotransformations by means of enzymes are continuous processes, as long as the reactor working life is longer than the native enzyme half-life, enzyme activity decay with time must be taken into account in order to correctly assess reactor performance.

The CSTR/UF reactor is useful for several types of reactions where a typical immobilized enzyme would not be effective.

Membrane Bioreactors with Membrane Used as a Separation Unit, Table 1 Most common membrane processes combined with reactions

Process	Driving force	Mode of transport	Species passed	Species retained
Microfiltration (MF)	Pressure difference	Size exclusion convection	Solvent (water) and dissolved solutes	Suspended solids, fine particulars, some colloids
	100–500 kPa			
Ultrafiltration (UF)	Pressure difference	Size exclusion convection	Solvent (water) and low-molecular-weight solutes (<1,000 Da)	Macrosolutes and colloids
	100–800 kPa			
Nanofiltration (NF)	Pressure difference	Size exclusion	Solvent (water), low-molecular-weight solutes, monovalent ions	Molecular weight compounds >200 Da multivalent ions
	chemical potential	Solution-diffusion		
		Donnan exclusion		
Forward osmosis (FO)	Concentration gradient	Solution-diffusion	Solvent (water)	Molecules, ions
	chemical potential			
Membrane distillation (MD)	Temperature gradient	Evaporation through nonwetting porous matrix	Vapor phase	Liquid phase
	vapor tension difference			
Membrane-based solvent extraction (MBSX)	Chemical potential or concentration difference	Diffusion partition	Compounds soluble in the extraction solvent	Compounds nonsoluble in the extraction solvent
Gas separation (GS)	Pressure difference	Solution-diffusion mechanism	Gas molecules having low molecular weight or high solubility-diffusivity	Gas molecules having high molecular weight or low solubility-diffusivity
	0.1–10 MPa			
Pervaporation (PV)	Chemical potential or concentration difference	Solution-diffusion mechanism	High permeable solute or solvents	Less permeable solute or solvents

Membrane Biosorption

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Biosorption, in the biological sense, is the ability of cells (usually microorganisms) to bind various substances in a passive way. Bioaccumulation of cells is the active retrieval from the environment

of certain components needed for life (i.e., metabolism). Biosorption can be achieved through a variety of specific mechanisms, where physical adsorption, ion exchange, and chemical reactions play a dominant role. Table 1 (below) shows the sorption capacity of various microorganisms such as bacteria, fungi, and algae.

Biosorption is also a new separation process (Volesky 1990) which depends on the concentration, temperature, pH, and sorbent properties that determine the equilibrium and kinetics. Cell debris may be also regarded as sorbents, which have even better sorption properties than whole cells because of greater sorption capacity (see

Membrane Biosorption, Table 1 Maximum uptake of heavy metals on various microorganisms

Type of biosorbent (microorganisms)	Heavy metal	Maximum uptake q^* (mg metal/g biomass)
<i>Bacillus subtilis</i> bacteria	Au	79
<i>Bacillus licheniformis</i> bacteria	Fe	45
<i>Aureobasidium pullulans</i> bacteria	Pb	220–360
<i>Citrobacter sp</i> bacteria	U	800
<i>Sargassum natans</i> algae	Au	400
<i>Chlorella vulgaris</i> algae	Au	80
<i>Sargassum natans</i> algae	Au	400
<i>Chondrus crispus</i> algae	Au	76
<i>Ascophyllum nodosum</i> algae	Cd	215
<i>Rhizopus arrhizus</i> fungus	Ag	54
<i>Rhizopus arrhizus</i> fungus	Au	164
<i>Streptomyces noursei</i> fungus	Ag	38
<i>Saccharomyces cerevisiae</i> fungus	Ag	5
<i>Saccharomyces cerevisiae</i> fungus	Cd	20–40
<i>Aspergillus niger</i> fungus	Au	176
<i>Penicillium chrysogenum</i> fungus	Cd	56

Membrane Biosorption, Table 2 The isotherms of biosorption equilibrium (Pagnanelli et al. 2003)

Isotherm	Equation
Langmuir	$q = q_{\max} \cdot \frac{b \cdot C}{1 + b \cdot C}$
Freundlich	$q = k \cdot C^{\frac{1}{n}}$
Langmuir–Freundlich	$q = q_{\max} \cdot \frac{b \cdot C^{\frac{1}{n}}}{1 + b \cdot C^{\frac{1}{n}}}$
Radke and Prausnitz	$\frac{1}{q} = \frac{1}{a \cdot C} + \frac{1}{b \cdot C^n}$
Redlich–Peterson	$q = \frac{a \cdot C}{1 + b \cdot C^n}$

Table 1) and rate of sorption (see Table 2). The smaller the particle size, the greater the surface areas and shorter diffusion paths for the molecules of xenobiotic (Koltuniewicz and Bezak 2002; Koltuniewicz and Witek 2004). Due to the special ability to bind heavy metals, biosorption process

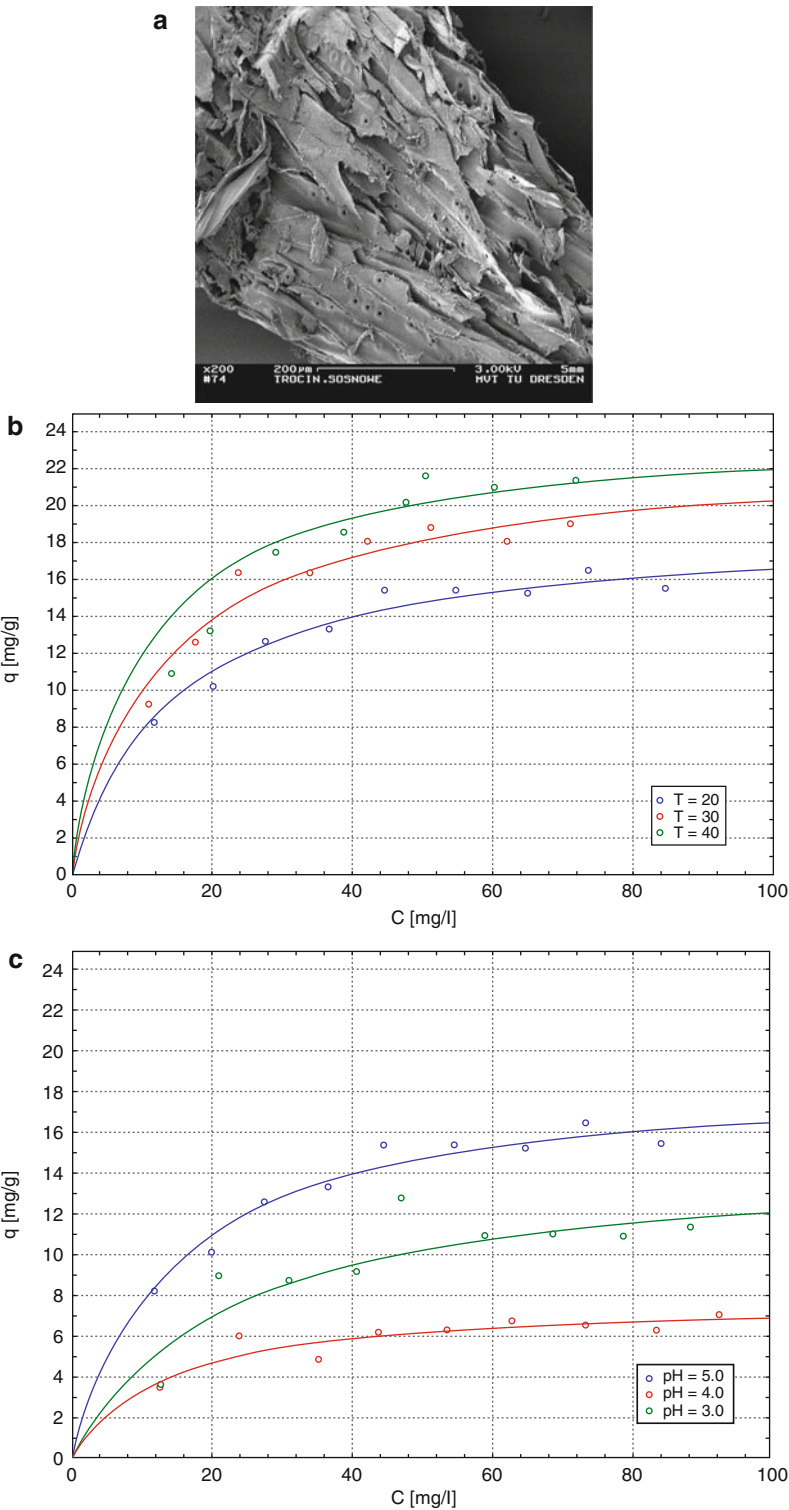
is currently used mainly in metalworking operations such as processing of ores, the production of batteries, power, thermal, and nuclear power generation, and some industrial wastewater treatment systems (Koltuniewicz and Drioli 2008; Koltuniewicz 2010). General examples of applications of biosorption are (I) removal of harmful substances from the environment and (II) separation of valuable substances from multicomponent mixtures. In the first case, the desired feature and the main value of biosorption are its low cost and widespread availability of biosorbents. Dealing with large amounts of contaminated water, which must be processed and, moreover, contains rather diluted substances to remove, such as heavy metals, organic substances or radioactive materials, is the biggest challenge for process engineering. In these cases, almost all methods of separation fail because their costs are rising dramatically. Therefore, the use of cheap biosorbents, which are often waste materials (algae, fungi, bacteria, sawdust, bark, etc.), may be helpful, especially for environmental protection.

In the second case (II), selective and specific sorbents with a high affinity for precious substances are sought. This method can also be useful to concentrate the atoms of noble metals such as gold, platinum and uranium, from industrial waste water, or even diluted in sea water.

In both cases, the use of membrane-assisted biosorption, namely, the “membrane biosorption,” may be recommended (Koltuniewicz and Bezak 2002). The membranes allow for easy concentration of finely ground biosorbents (Fig. 1) or cells (Fig. 2), which is impossible in the thick layer of packed columns. Very fine grinding is desirable because of the possibility of increasing the surface of sorption and shortening of the diffusion paths to active sites. This increases the efficiency of sorption, even in dilute suspensions. However, the costs of milling and additional operations such as drying, sorting, etc. should always be taken into account. So in order to make real use of biosorption, the calculations must be performed in any case. The next part shows the equations needed to calculate the membrane biosorption process.

Membrane Biosorption,

Fig. 1 Equilibrium adsorption of copper ions to the pine sawdust (a). Effect of temperature (b) and pH (C). (A) Photomicrograph of pine sawdust used for the biosorption of copper ions. (B) Effect of temperature on biosorption of copper ions on the sawdust. (C) Effect of pH on biosorption of copper ions on the sawdust





Membrane Biosorption, Fig. 2 Microorganisms on the membrane surface

Membrane Biosorption, Table 3 Kinetic equation of the biosorption (Pagnanelli et al. 2003)

Reaction type	Equation
First-order reaction	$q(t) = q^* \cdot (1 - e^{-k \cdot t})$
Pseudo-second order reaction	$q(t) = \frac{1}{\frac{1}{k \cdot q^*} + \frac{t}{q^*}}$

Membrane Biosorption, Table 4 Experimentally determined constants m and n in correlation between rate of surface renewal and average cross-flow velocity in different types of modules (Koltuniewicz 1995)

Module type	Constant – m	Constant – n
Plate and frame (slot 0.15 × 0.001 m)	0.00074	0.75
Tubular ceramic (Membralox® 19 tubes)	0.0020	0.80
Capillary (Romicon®, d = 1 mm)	0.0035	0.66

Calculations of Membrane Biosorption Process

The obvious drawback of membrane biosorption is the quick saturation of the thin layer of biosorbent on membrane surface is rapidly progressing with time, until equilibrium is reached. The equations describing the equilibrium and kinetics for biosorption process can be determined on the basis of experimental data (see Tables 1, 2, 3, and 4 in Fig. 1).

The concentration in the biosorbent (q) varies with time, due to its saturation with solute (i.e., xenobiotic), which can be expressed in the formula:

$$q(t) = q^* - (q_0 - q^*) \cdot e^{-kt}$$

Where:

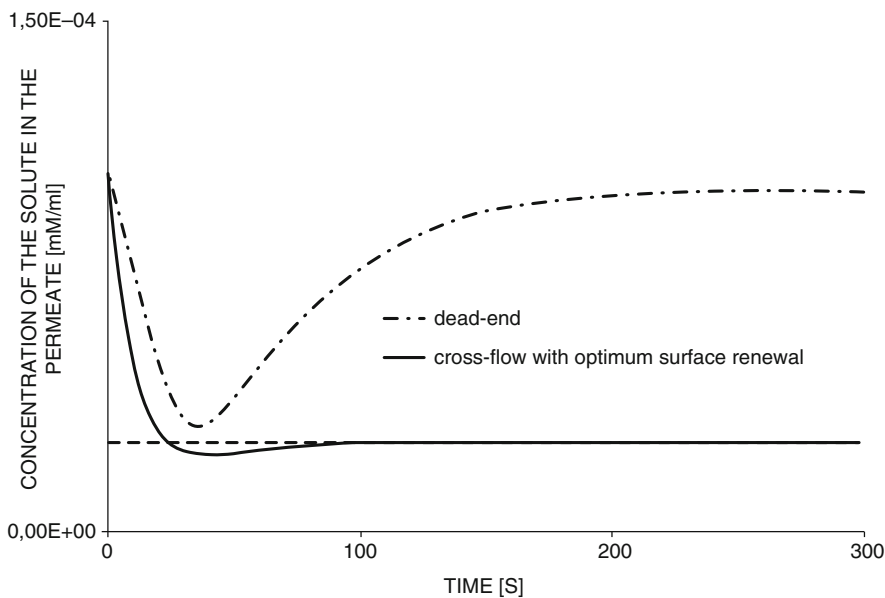
- $q(t)$ [kg_{solute}/kg_{biosorbent}] – solute (xenobiotic) concentration in the biosorbent
- q^* – equilibrium value of solute concentration in the biosorbent (maximum uptake see Table 1)
- q_0 – initial solute concentration in the biosorbent, e.g., solute concentration in the sorbent which is supplied with the feed

During dead-end mode of operation, when the unaffected biosorbent lies on the membrane surface, and the liquid passes through its layer, the concentration in the fluid changes according to equilibrium. Change of concentration over time in the permeate stream can be then calculated from the mass balance (see Fig. 3) (Koltuniewicz and Bezak 2002; Koltuniewicz and Witek 2004). The balance of xenobiotic in an open system, during the flow of fluid through a layer of biosorbent, permeates flow results in a superposition of two effects: (1) the tendency to reduce the concentration of xenobiotic in the permeate due to its biosorption and (2) the tendency to increase the concentration as a result of inflow of xenobiotic, with the liquid. Thus, the relationship has a minimum of the xenobiotic concentration in the permeate after biosorption:

$$C_P(t) = C_R - \frac{k \cdot X_m \cdot \delta \cdot (q^* - q_R)}{J - k \cdot \delta} \cdot \left[e^{-kt} - e^{-\frac{J}{\delta}t} \right]$$

Where:

- $C_P(t)$ – instantaneous concentration of solute in the permeate
- C_R [kg_{solute}/m³_{retentate}] – constant concentration of solute in the retentate inflow,
- X_m [kg_{biomass}/m³_{retentate}] – average biomass concentration on the membrane surface



Membrane Biosorption, Fig. 3 Purity of permeate after the process of membrane biosorption in dead-end and cross-flow modes of operation

δ [m] – thickness of the sorbent layer on the membrane

k [s^{-1}] – biosorption kinetic constant

q_R [$kg_{\text{solute}}/kg_{\text{biomass}}$] – solute concentration in the sorbent in the retentate

q^* – maximum uptake, i.e., equilibrium value of the solute concentration in the sorbent

J [m^3/m^2s] – permeate flux

t [s] – real time of the process

It should be underlined that sorption process in dead-end mode is unpractical because of very small volume of active biosorbent layer at the membrane surface. Therefore, to maintain stationary conditions of the process, some way to remove the thin active layer of sorbent from the membrane surface after appropriate process time must be found. Duration, after which the concentration of solute in the permeate is the minimum, may be selected as a time of the periodic back flushing and can be calculated from the formula:

$$t(C_P^{\min}) = \frac{\ln\left(\frac{k\delta}{J}\right)}{k - \frac{J}{\delta}}$$

Methods to reduce the concentration polarization layer are well known in the membrane processes to maximize the permeate flux. They are turbulences or shear forces, shear-induced diffusion, lifting forces, pinch effects, lateral migrations, scouring effects, gas sparging, etc. We can now apply them for controlled renewal of a biosorbent film from the surface of the membrane by using hydrodynamic effects during cross flow. Application of Danckwerts model allows to determine the optimal rate of surface renewal (Koltuniewicz and Witek 2004).

$$s_{opt} = \sqrt{\frac{k \cdot J}{\delta}} \text{ for } C_P^{\min} \text{ when } \frac{dC_P^m}{ds} = 0$$

The optimal conditions for renewing the surface we get when the lowest concentration of the xenobiotic in the permeate (i.e., the highest possible purity) of cross-flow conditions can be achieved. This is when the frequency of renewal of the sorbent film(s) is synchronized with the (i) flow of permeate “ J ,” (ii) thickness of the sorbent layer on the membrane “ d ,” and (iii) the kinetics of sorption “ k ” (see Fig. 1). Then the average concentration in the permeate outflow from the entire

surface of the membrane (i.e., the sum of the concentrations in the streams flowing from all of

its components) can be expressed by the formula (see also Fig. 3 at continuous line):

$$C_P^m = C_R - \left[\frac{1 - e^{-(k+s) \cdot t_p}}{k + s} - \frac{1 - e^{-\left(\frac{J}{\delta} + s\right) \cdot t_p}}{\frac{J}{\delta} + s} \right] \cdot \frac{k \cdot X_m \cdot \delta \cdot (q^* - q_R)}{J - k \cdot \delta} \cdot \frac{s}{1 - e^{-s \cdot t_p}}$$

After the long duration of process, this concentration becomes constant, leveling off on the asymptotic value independent on time of the process t_p (see Fig. 1 dashed line).

$$C_P^m = C_R - X_m \cdot (q^* - q_R) \cdot \frac{k \cdot \delta \cdot s}{(J + s \cdot \delta) \cdot (k + s)}$$

The rate of the surface renewal depends on many hydrodynamic parameters and must be determined experimentally. However, rough estimates assuming close to the water systems can use a simple exponential dependence on average velocity retentate at different membrane modules, which were presented in Koltuniewicz (1992).

$$s = m \cdot u^n$$

All the above data and formulas can be very helpful in practical use of opportunities and potential of membrane biosorption as a new separation process.

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Membrane Biotechnology

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Synonyms

[Biotechnology processes coupled with membrane separation](#); [Integration of membrane separation with biotechnology](#)

Introduction

Membrane biotechnology is the integration of membrane separation with biotechnology and has been widely used in various biotechnology processes, e.g., reaction, separation, clarification, and recovery. Membrane separation is very suitable for biological processes since it is usually operated at mild temperatures and pressures and requires no phase changes or chemical additives, thereby minimizing the extent of denaturation, deactivation, and/or degradation of biological products (Charcosset 2006). The sterile filtration of fermentation media, purification buffers, and protein product pools is a standard practice in

industry, and high-resolution applications of membrane separation in biotechnology processes for improved protein-virus separation, protein purification by high-performance tangential-flow filtration, and enhanced membrane chromatography are also targeted (van Reis and Zydney 2001).

Membrane biotechnology includes membrane separation process, membrane bioreactor, membrane chromatography, membrane contactor, and other combined processes. Membrane separation processes are utilized to recover macromolecules and retain suspended solids and solutes of large molecular weight. Typical membrane separation processes are microfiltration, ultrafiltration, nanofiltration, and reverse osmosis filtration. Novel separation processes, e.g., forward osmosis and membrane distillation, have been also developed. Applications of membrane separation include sterile filtration (bacterial removal), clarification of fermentation broths, product concentration and recovery, antibiotic production, biorefineries, renewable fuel production, and so on (Charcosset 2006; Huang et al. 2008; Addehagh et al. 2014).

Membrane bioreactors (MBRs) combine activated sludge processes with advanced membrane separation. Current available commercial MBR processes employ the membrane ostensibly as a filter, rejecting the solid materials or solutes with large molecular weight developed by the biological process to provide a clarified and disinfected product (Judd 2011). MBR types are generally divided into several categories based on the purpose of membrane usage: biomass separation membrane bioreactor (BSMBR), membrane aeration bioreactor (MABR), extractive membrane bioreactor (EMBR), and ion-exchange membrane bioreactor (IEMBR) (Stephenson et al. 2000; Gu and He 2002; Oehmen et al. 2006). BSMBR, usually termed as MBR (see the related term, MBR), is the most prevalent among the different types (Wang et al. 2008).

Membrane chromatography is used as an alternative to conventional resin-based chromatography columns, for a large range of chromatographic purification schemes, including ion-exchange, hydrophobic, reversed-phase, and affinity chromatography. Membrane materials for chromatographic applications include cellulose, polysulfone, polyamide, hydrazide, and composite

membrane such as blend of polyethersulfone and polyethylene oxide coated on all surfaces with a covalently bound layer of hydroxyethylcellulose (Charcosset 1998). Commercial membranes include flat sheet systems (Pall, New York), membrane stacks (Sartorius, Göttingen, Germany), radial-flow cartridges (CUNO Europe, Cergy-Pontoise, France), and hollow-fiber modules (Kinetic Systems Inc., St. Louis, MO) (Charcosset 2006).

Membrane contactor can be defined as the connection of two phases A and B through membrane pores. Membrane distillation involves a temperature gradient to promote water vapor to permeate through a porous hydrophobic membrane. Membrane emulsification involves using a pressure to force the dispersed phase A to permeate through a membrane into the continuous phase B, which flows tangentially to the membrane surface. Membrane pores act as parallel capillaries for the introduction of phase A into phase B. Membrane contactors are applied for the preparation of emulsions (membrane emulsification) and for the preparation of crystals (membrane crystallization).

Membrane separation can be also integrated into other novel processes. For example, membrane separation has been used in microbial fuel cells (MFCs), which use bacteria as the catalysts to oxidize organic and inorganic matter and generate current. In a typical MFC, a cation-exchange membrane (CEM) is applied to separate the anode and cathode compartments, through which protons in the system can migrate (Logan et al. 2006).

The membrane properties could be further enhanced by the modification of its physicochemical characteristics (e.g., porosity, hydrophilicity, zeta potential, and pore size) to improve the efficiency in reaction, separation, clarification, and recovery schemes (Wang et al. 2013). The rapid development in membrane technology will allow membranes to play an important role in the evolution of the next generation of biotechnology processes.

Cross-References

- [Membrane Bioreactors for Treatment of Tannery Effluents](#)
- [Ultrafiltration Membrane Bioreactor](#)

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Membrane Capacitive Deionization

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Membrane capacitive deionization, MCDI, is a technology for water desalination based on the use of an assembly of a spacer channel, two ion exchange membranes, and two porous carbon

electrodes. Of the two electrodes, one is the cathode, in which cations are adsorbed during desalination, and the other is the anode. In front of the cathode, a cation exchange membrane is placed, while an anion exchange membrane is placed in front of the anode. MCDI is a cyclic process, in which for some time freshwater is produced, followed by a period in which a concentrate stream leaves the device. To increase water recovery, the second period (ion release) must be short relative to the first period (ion adsorption).

In MCDI, upon transferring electrical charge from cathode to anode, against a cell voltage difference opposing this electrical charge transfer, the ions are removed from the water flowing through the spacer channel and are adsorbed in their counter electrode. In this way water is obtained which is desalinated to a certain degree. After some time, the electrodes have reached their adsorption capacity, and the electrical current is reversed, thereby releasing the ions from the electrodes, leading to a stream of brine (concentrate) flowing from the device.

As each layer in the assembly is about 100–300 μm of thickness, a complete cell, including also “graphoil” current collectors on either side, is about 1.0–2.0 mm of total thickness. Thus, in a “stack” of 10 cm of height, it is possible to pack up to 100 of such cells. The current collectors serve to inject the electrical current from the external circuit into the porous electrodes, which are accessible for the water and the ions. Ion storage is based on the formation of electrostatic double layers within the nanopores in the carbon electrode particles, where electrical charge is locally charged compensated by counterions.

The advantage of MCDI over the related technology without membranes, CDI, is that during the charging or desalination step, co-ions (ions of the same charge sign as the electrode) are blocked from leaving the electrode region. This effect does occur in CDI and limits the charge efficiency, i.e., the amount of salt molecules removed from the water per amount of charge transferred. A second advantage of MCDI is that upon reversing the voltage during cell discharge, it is possible in MCDI to completely remove all counterions from their electrode, thereby increasing the desalination capacity in a next cycle.

Cross-References

- [Characterization of Porous and Dense Membranes](#)
- [Ion-Exchange Membrane Characterization](#)

Membrane Charge

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Membrane charge: Membranes acquire a characteristic electric surface charge when contacted with an aqueous solution. For both organic and inorganic membranes, the surface of a membrane can become charged due to the dissociation of specific ionizable groups on the surface. These ionization reactions depend on the pH and the electrolyte in the bulk solution in contact with the membrane. The charge and resulting potential of the membrane depend strongly on the pH of the system because the majority of the membrane functional groups protonate and deprotonate over the pH range.

As a direct result of the fabrication materials traditionally employed in membrane manufacture, most membranes are either neutral or negatively charged in an aqueous processing environment (Tsuru et al. 1998; Childress and Elimelech 1996). However, positively charged membranes can be produced by surface modification of the membrane (Cheng et al. 2011). The most common technique for evaluating the membrane surface charge (zeta potential) is via streaming potential measurements (Hunter 1981).

The charge of the membrane is significant to membrane performance because charge affects the electrostatic repulsion between the ions or charged molecules and the membrane surface. This can also have an impact on membrane fouling as well.

Cross-References

- [Surface Charge Density](#)

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Membrane Charge (Zeta Potential) Effect

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Membrane surface charge (zeta potential) effect: The membrane surface charge or zeta potential is most often characterized using the streaming potential method (Hunter 1981) (see “► [Membrane Charge Characterization](#)”). The charge of a membrane is significant to membrane performance because charge affects the electrostatic repulsion between the ions or charged molecules and the membrane surface.

Due to the materials used in the fabrication of membranes, most membrane surfaces show a negative charge at neutral pH values (i.e., pH 7). However, due to the amphoteric nature of the chemical groups on the surface of a membrane, the charge may be altered by adjusting the solution conditions (i.e., pH and electrolyte concentration) (Cheng et al. 2011). Surface modifications may also be made to membranes in order to change the charge from negative to positive (Cheng et al. 2011; Kobayashi et al. 1996).

Membrane surface charge has a big influence on the rejection of charged species (i.e., salt, charged dyes, amino acids, etc.) for nanofiltration membranes. The isoelectric point (Hunter 1981)

(the pH at which point where there is no effective charge) of a membrane can be determined from the minimum rejection value obtained when filtering a charged species (like sodium chloride (NaCl)), by varying the pH value at a fixed electrolyte concentration and constant applied pressure (Cheng et al. 2011).

For ultrafiltration membranes, the charge on the membrane surface will affect the interactions between the membrane and the particles in the feed solution. If the charge on both the membrane surface and the particles is of the same sign, repulsion will occur, and there will be less fouling and concentration polarization at the membrane surface. However, if the charge on the membrane surface is of the opposite sign to the particles, attractive forces will dominate and the membrane will foul easily, thus reducing performance. The membrane charge can have a significant effect on the flux obtained (Bacchin et al. 2006).

The determination of the membrane surface zeta potential can also be used as an indicator for membrane fouling (Lawrence et al. 2006; Al-Amoudi et al. 2007). The effect of foulants can be investigated, and based on the measurement results, the membrane surface can be specifically treated to decrease membrane fouling and extend the membrane lifetime (Lawrence et al. 2006; Al-Amoudi et al. 2007).

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Membrane Charge Characterization

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The surface charge density and thus membrane charge of a porous membrane are related to the zeta potential of the membrane. There are several procedures that allow characterization of the membrane zeta potential and thus surface charge.

Streaming Potential

When an electrolyte solution flows across or through a stationary, charged membrane, the flow of liquid tangential to the material drags the excess charges near to the material wall downstream. This causes the build-up of an electric field which drives a current in the reverse direction. The streaming potential that is induced may be measured using electrodes. The zeta potential is calculated from the measured streaming potential using the Helmholtz-Smoluchowski equation (Smoluchowski 1905; Abramson 1934) with the Fairbrother and Mastin substitution (Fairbrother and Mastin 1924). The streaming potential may be measured either across the surface of the membrane, by forming a thin channel and pumping the electrolyte through this channel, or through the pores enabling measurement of the streaming potential across the membrane (Nystrom et al. 1994).

Electroosmosis

A simple “dipped cell” apparatus can be used for measuring the electroosmotic flow rate across a microporous membrane (Bowen and Clark 1984).

The membrane is held at the end of a deep tube immersed in the thermostated electrolyte. Two electrodes are used. The first one is positioned behind the membrane and the second one is positioned outside the tube. At the beginning of the experiment, the liquid level both inside and outside the tube are the same. A constant current is then applied between the two electrodes which induces an electroosmotic flow of electrolyte in the tube. Overflowed electrolyte is transferred to an electronic balance. Zeta potential was determined by measuring the rate of electroosmosis across the membrane.

The literature shows that the streaming potential method has been much more widely studied in comparison to electroosmosis phenomena.

For nanofiltration membranes, it is also possible to evaluate the effective membrane charge density, X_d , by fitting experimental data of the variation of electrolyte rejection with concentration (Bowen et al. 1997). However, this parameter is essentially a fitting parameter and has no real physical basis.

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Membrane Classification

► Membrane (Definition, Function, Structure)

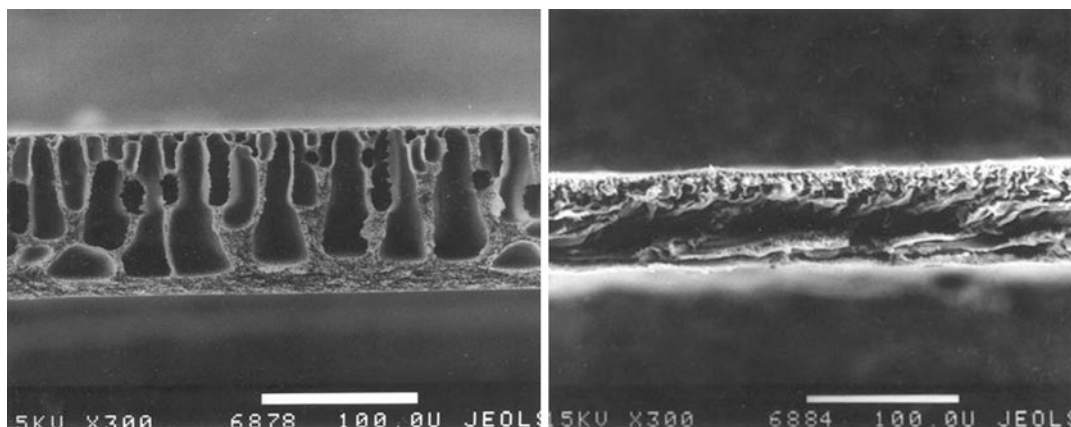
Membrane Collapsing

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Membrane collapsing is irreversible changing in the membrane structure (porous structure) as a result of external factors. Membrane collapsing is mostly typical for the membranes with a porous structure that artificially forms during the membrane casting (e.g., by phase inversion). Membrane collapsing can take place mainly in two following cases: (i) drying or non-proper replacement of solvent/non-solvent contained in the membrane and (ii) high transmembrane pressure that exceeds mechanical stability of used membrane material. The former one is mostly typical for NF or RO membranes. To preserve a fine (porous) structure of selective layer, RO/NF membranes are commonly impregnated by non-volatile solvent like glycerin or supplied in a wet state (in preserve solution) (Mallevalle and Odendaal 1996). Once the membrane is dried, the membrane cannot retrieve its initial filtration characteristics due to dramatic irreversible changes within the structure of selective layer. Therefore, the membranes are installed in a wet state and then preserve agent is washed out during filtration of pure water (membrane pretreatment). If the membrane should be operated in nonaqueous media, it is recommended to replace the preserve solution by a number of solvents or its mixtures in order to provide step-wise change of solvent surface tension. Non-proper solvent exchange could lead to noticeable deviation in membrane performance (Volkov et al. 2008).

Since the porous structure of the selective or support layers could have a limited mechanical stability, the membrane manufacturers usually provide the information about the maximum transmembrane pressure at which the membrane still exhibits the claimed characteristics. It should



Membrane Collapsing, Fig. 1 Collapsing of membrane porous structure: initial membrane (*left*), collapsed membrane after TMP of 20 bar (*right*)

be mentioned that increase of polymer segments mobility (e.g., transition from glassy to rubbery state) or membrane swelling (polymer plasticization) may also lead to membrane collapsing; it is commonly observed for high-pressure gas separation or organic solvent nanofiltration (Nunes and Peinemann 2006). Figure 1 illustrates typical example of collapsing of membrane porous structure as a result of applying of high transmembrane pressure that exceeds the mechanical stability of the support layer.

In a case of the polymer with intrinsic microporosity, the change in porous structure is referred as partial relaxation of free-volume structure also called as a physical aging. Membrane can be also collapsed as a whole construction if high pressure is applied on shell side (outside) of hollow fiber membrane.

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Membrane Compaction

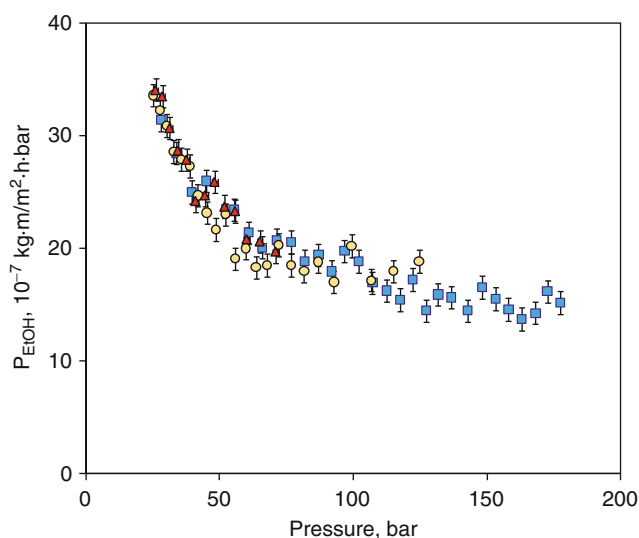
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Membrane compaction can be considered as a compression of the membrane under applied pressure resulting in decline of transport characteristics of the membrane. Membrane compaction is quite commonly observed phenomena, especially decrease of initial membrane transport parameters in pressure driving processes like gas separation or membrane filtration. Typically, increase pressure drop across the membrane leads to more pronounced effect of membrane compaction. If the membrane is already compacted at the operated pressure, steady-state performance can be expected. However, the flux decline over the time can be also attributed to membrane fouling, which is known as a partial blockage of membrane surface and/or pores inside of the membrane by components of the feed. Unfortunately, it is difficult to distinguish the effect of membrane compaction from membrane fouling, especially, during the operation with multicomponent mixtures.

Membrane Compaction,

Fig. 1 Effect of reversible membrane compaction on the ethanol permeability through dense membrane of PTMSP: three filtration series in which the transmembrane pressure was reduced from 200 (■), 150 (●), or 100 bar (▲), respectively (Grekhov et al. 2012)



For minimization of the time required for preliminary membrane compaction, it is recommended to start experiment with the highest pressure and then stepwise decrease the transmembrane pressure. Membrane compaction cannot be avoided, but its effect on membrane performance can be controlled; moreover, the initial membrane compaction has a greater impact on the membrane. From this end, the membrane manufactures quite often provide the protocol of preliminary membrane conditioning that has to be followed in order to guarantee claimed membrane characteristics.

Membrane compaction as a physical compression can have reversible, partially reversible or irreversible effect on membrane structure. The membrane collapsing is one of the examples of irreversible membrane compaction, and this effect is attributed to mechanical destruction of porous structure of the membrane as a result of applied pressure. Increase of polymer segment mobility (e.g., transition from glassy to rubbery state) or membrane swelling (polymer plasticization) may also lead to more pronounced effect of membrane compaction under applied pressure; it is commonly observed for high-pressure gas separation or organic solvent nanofiltration (Nunes and Peinemann 2006). Figure 1 illustrates an example of reversible membrane compaction, when the membrane is recovering its transport properties

with a decrease of the transmembrane pressure; as can be seen, the normalized liquid permeability is a function of pressure here.

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Membrane Condenser

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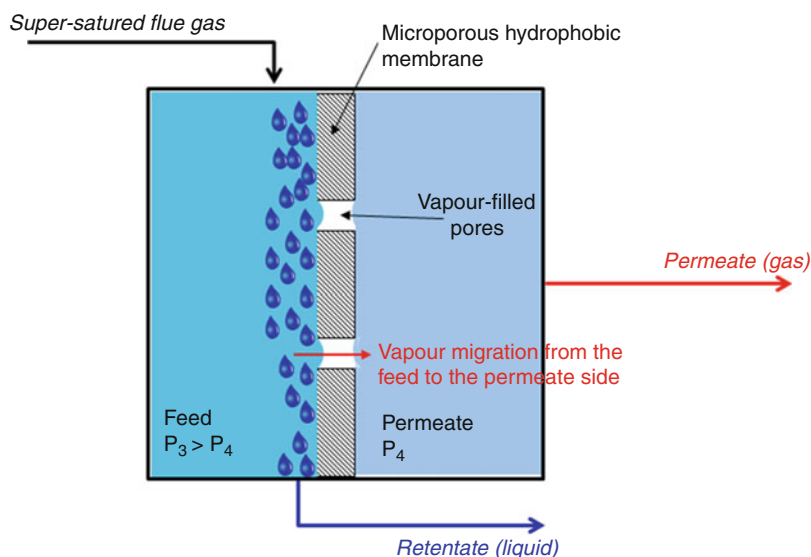
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The selective recovery of evaporated wastewater from industrial gases can be carried out through membrane condensers.

Membrane Condenser,

Fig. 1 Scheme of the membrane condenser process for the recovery of evaporated “waste” water from flue gas as feed



The principle of working of this new membrane technology has been recently introduced by Macedonio et al. 2013 and consists in condensing and recovering the water contained in a saturated gas on the retentate side of a membrane module, by exploiting the hydrophobic nature of the membrane, whereas the dehydrated gases pass through the membrane in the permeate side.

Figure 1 schematizes the membrane condenser principle.

The gaseous stream (e.g., flue gas) exiting from the power plant, cooling towers, stacks, etc. at a certain temperature and relative humidity is fed to the membrane condenser kept at a lower temperature for cooling the gas up to a supersaturation state. The water condenses in the membrane module once this stream is brought into contact with the retentate side of the microporous membranes; the hydrophobic nature of the latter prevents the penetration of the liquid into the pores letting pass the dehydrated gases through. Therefore, the liquid water is recovered at the retentate side, whereas the other gases at the permeate side of the membrane unit. In comparison with the traditional technologies, the membrane condenser is characterized by various aspects that differ them from the others (Table 1).

At first, they offer higher water recovery with respect to all the other technologies. In addition, despite the adsorption units where problems related to desiccant losses or corrosion can occur, the membrane condensers can be considered as a clean unit operation. However, whether the gaseous stream contains ashes or particles, a pretreatment stage could be required before feeding the membrane condenser. Compared with the dense membrane technology, the main difference can be found in the operating conditions and in the water quality. To promote the permeation of water vapor through dense membranes, a high pressure difference between the two membrane sides is required, implying investment and operational costs related to the presence of compressors or vacuum pump. On the contrary, the purity of the water recovered in membrane condensers can be affected by the possible condensation of contaminants – if present in the gaseous stream – but it is sufficient for cooling tower or boiler makeup. In this context, the possibility of controlling, by opportunely tuning the operating conditions, the condensation of contaminants in the liquid water recovered in the retentate side of the membrane condenser could lead to two different options for its use: as a unit for water recovery,

Membrane Condenser, Table 1 Comparison between membrane condenser and traditional technologies (Brunetti et al. 2013)

	Liquid and solid sorption (Ito 2000)	Cooling with condensation (Folkedahl et al. 2006)	Dense membranes (Isetti et al. 1997)	Membrane condensers (Brunetti et al. 2013)
Water recovery	22–62 %	<70 %	20–40 %	>70 %
Water purity	>95 %	Sufficient for cooling tower makeup	>95 %	Sufficient for cooling tower makeup
		Contaminants in the water		Contaminants in the water
Maintenance and durability	Corrosion and salt crystal formation owing to salt desiccants' presence and O ₂ in the flue gas	Corrosion owing to the formation of a thin liquid layer of diluted acids and fly ashes forming deposits	Ashes removal and FGD necessary to avoid membrane damaging	Ashes removal to avoid membrane damaging
Environmental aspects	Increase of CO ₂ emissions	Co-capture of SO _x and NO _x could result in an environmental profit reducing the DENOX and FGD systems	Clean operation	Clean operation
	Reduction of SO _x emission			
	CaCl ₂ losses			
Investments costs	\$5.8 million (2006) +200,000 \$/year (2006) as operational costs	6.4 million euros (2011)	To be determined	To be determined
Economic viability	4.4 \$/m ³	1.5–2 euro/m ³	1.5 euro/m ³ (wet regions)	1.5–2.5 euro/m ^{3a}
			10 euro/m ³ (dry regions)	

^aConsidering only costs related to energy requirements and membrane modules

minimizing the contaminants content, or as the pretreatment stage in post-combustion capture, forcing most of the contaminants to be retained.

As for the well-known membrane contactors of which membrane condensers represent a special category, many are the challenges that still limit their scaling up from laboratory to industry level.

First of all, the fundamental property that the membrane used in membrane condensers has to show is the high hydrophobicity that avoids the penetration of condensed water into the membrane pores and thus favors the separation of liquid phase from the gaseous one recovered on the permeate side. The hydrophobic character of these membranes is influenced, without any doubt, by the feed conditions. As aforementioned,

in most of the cases, the waste gaseous streams coming out from chimneys of industrial plants contain variable amount of contaminants such as SO_x, NO_x, NH₃, HF, HCl, etc. that on a long-term basis could affect the performance of the membrane condenser, depleting the hydrophobic character of the membrane. The challenge is, thus, to identify materials for making membranes that exhibit excellent resistance and stability toward these components. Actually, these are well represented by PVDF or other superhydrophobic materials such as Hyflon, Teflon, etc. that have the only disadvantage to be quite expensive. The synthesis of new composite membranes where the hydrophobic layer is deposited on a cheaper support can lead to the long-term stability together with a reasonable cost of the unit.

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Membrane Contactor (MC)

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Membrane contactors are membrane-based devices that are used to carry out many unit operations like gas–liquid mass transfers, liquid–liquid extractions, and distillation (Drioli et al. 2006). The membranes employed can be both hydrophobic and hydrophilic and their pore size usually ranges from 0.05 to 1 μm . The role of the membrane is to put in contact the involved phases, and the separation is not due to its selectivity, as in the

other membrane operations, but the mass transport occurs at the interface, where the two phases are in contact. In particular, hydrophobic membranes are able to block at their surface polar phases, whereas hydrophilic membranes prevent the passage of nonpolar ones (Fig. 1a, b).

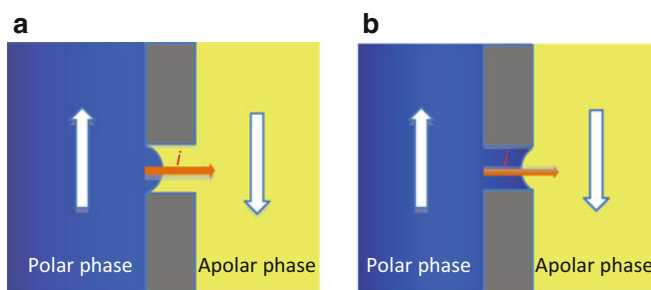
Being each micropore a point of contact for the phases, and being the number of micropores in one membrane extremely high, one of the main advantages of this system, with respect to conventional operations, is the high interfacial area available in small volumes. Furthermore, the possibility of having the interface established at each micropore results in a more stable and better contact between phases. However, for ensuring that no mixing of phases occurs, it is mandatory to do not exceed the so-called breakthrough pressure, that is, the value of pressure at which the phase blocked at the pore mouths starts to penetrate inside the pores. The value of the breakthrough pressure depends on different parameters, like the membrane pore size, the degree of hydrophobicity of the membrane surface, and the fluid properties and can be calculated by Laplace’s equation:

$$\Delta P = (-2\sigma \cos\theta)/r$$

with σ , surface tension of liquid; θ , contact angle between the liquid and the membrane; and r , membrane pore radius.

Different are the membrane operations that belong to the “membrane contactors family” like membrane strippers and scrubbers, supported liquid membranes, phase transfer catalysis, and membrane and osmotic distillation.

Membrane Contactor (MC), Fig. 1 Interface in a hydrophobic (a) and hydrophilic (b) membrane contactor and transport of the species i through the membrane micropore



Membrane Contactor (MC), Table 1 Main advantages and drawbacks of membrane contactors

Main advantages	Main drawbacks
High compactness	Membrane resistance to the mass transport
Known and stable interfacial area	Membrane fouling and loss of membrane properties (like hydrophobicity)
No need of units downstream for phases separation	Operating pressures dependent on the breakthrough pressure value
Flexibility and modularity	

Table 1 summarizes the main advantages and drawbacks of membrane contactors.

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Membrane Crystallization (MCR)

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Membrane operation is aimed at promoting the formation of crystals from supersaturated solutions. The concept of membrane crystallization combines the principles of mass and heat transport through membranes with the theory of heterogeneous nucleation occurring at the interface with polymeric films (Drioli et al. 2005).

Crystallization from solution is driven by supersaturation S , defined as the ratio between the actual solute concentration c and the equilibrium value c^* (saturation):

$$S = \frac{c}{c^*} \quad (1)$$

The selective removal of solvent through appropriate membranes is used to increase the concentration of the solute up to the required supersaturation. Alternatively, membranes are used to selectively feed an antisolvent to induce a demixing effect that generates supersaturation.

Mass transport depends on the specific typology of employed membranes: for microporous hydrophobic membranes (mass transfer in vapor phase under temperature and/or concentration gradient) Dusty Gas Model is applied; for thin film composite membranes (mass transfer in liquid phase under pressure or concentration gradient), Solution-Diffusion Model is employed.

Morphological and physicochemical parameters of the membranes, such as porosity, roughness, or hydrophilic/hydrophobic character, affect significantly the nucleation kinetics. In fact, the formation of a critical nucleus (having 50 % probability to grow or dissolve) is an activate process that imposes the necessity to overcome a Gibbs energy barrier ΔG^* that, for homogeneous nucleation occurring in the bulk of the solution, is given (according to the Classical Nucleation Theory (Drioli et al. 2015)) by:

$$\Delta G_{\text{homogeneous}}^* = \frac{16}{3} \pi \gamma_L^3 \left(\frac{\Omega}{\Delta \mu} \right)^2 \quad (2a)$$

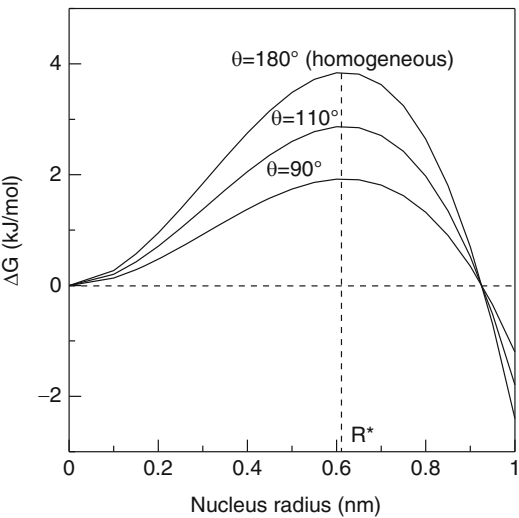
where γ_L is the surface tension of the nucleus-liquid interface, Ω the molar volume of the solute, and $\Delta \mu$ the chemical potential gradient between the crystalline phase and the mother solution. The corresponding critical nucleus R^* is given by:

$$R_{\text{homogeneous}}^* = \frac{2\gamma_L \Omega}{\Delta \mu} \quad (2b)$$

Membrane surfaces act as a promoter of crystallization by lowering the activation barrier to the nucleation stage, thus allowing molecules to aggregate in conditions of supersaturation that would not be adequate for the spontaneous nucleation; therefore, the rate of generation of nuclei is increased. In order to evaluate quantitatively this effect, a constitutive relation expressing the mechanical equilibrium between nucleus-solution (γ_L), nucleus-membrane (γ_i),

Membrane Crystallization (MCr), Table 1 Critical nucleus (R^*) and Gibbs free energy ratio between heterogeneous and homogeneous nucleation ($\Delta G_{\text{heterogeneous}}/\Delta G_{\text{homogeneous}}$) as a function of physicochemical parameters of the membrane

Parameter	R^*	$\Delta G_{\text{heterogeneous}}/\Delta G_{\text{homogeneous}}$
Contact angle (θ), ideal surface	$\frac{2\gamma_L\Omega}{\Delta\mu}$	$(\frac{1}{2} - \frac{3}{4}\cos\theta + \frac{1}{4}\cos^3\theta)$
Porosity (ε)	$\frac{2\Omega\gamma_L}{\Delta\mu} \left[1 - \varepsilon \frac{(1+\cos\theta)^2}{(1-\cos\theta)^2} \right]$	$\frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2 \left[1 - \varepsilon \frac{(1+\cos\theta)^2}{(1-\cos\theta)^2} \right]^3$
Wenzel roughness (r)	$\frac{2\Omega\gamma_L}{\Delta\mu} Y$ $Y = \frac{r \cos\theta(1+\cos\theta)-2}{\cos\theta(1+\cos\theta)-2}$	$\frac{1}{4}Y^3(\cos^3\theta - 3\cos\theta + 2)$



Membrane Crystallization (MCr), Fig. 1 Gibbs free energy versus nucleus radius at three different contact angles ($\theta = 90^\circ, 110^\circ, 180^\circ$). Curves reach a maximum in correspondence of the critical radius R^* . Input data: $c/c^* = 1.5$; $\Omega = 1.9 \cdot 10^{-28} \text{ m}^3$; $\gamma_L = 0.004 \text{ J/m}^2$

and solution-membrane (γ_s) interfaces is required. For an ideally solid and smooth surface, Young equation gives:

$$(\gamma_s - \gamma_i) = \gamma_L \cos \theta \tag{3}$$

The introduction of (Eq. 3) into the energy balance of the crystalline phase allows evaluating the reduction of ΔG^* for nuclei formed on a flat sheet membrane. The values of $\Delta G_{\text{heterogeneous}}/\Delta G_{\text{homogeneous}}$ for this case, as well as for porous or rough membranes, are reported in Table 1.

Figure 1 shows that, if nucleation occurs on polymeric membrane with $\theta < 180^\circ$, the work required to generate a critical nucleus on the

surface is higher with respect to nucleation in the bulk of the mother solution ($\theta = 180^\circ$). This phenomenon is known as heterogeneous nucleation.

The possibility to modulate the nucleation rate as a function of morphological and physicochemical properties of the membranes allows to redirect the selective formation of stable or metastable polymorphs. Although identical in their chemical composition, different polymorphs often exhibit important differences in solubility, dissolution rate, stability, melting point, density, and many other properties that significantly affect the efficacy, bioavailability, and safety of active pharmaceutical ingredients. Polymorph selection by membrane crystallization was confirmed by experimental tests carried out on: glycine (selective crystallization of forms α and γ), paracetamol (possibility to discriminate between the monocline stable form of polymorph I and the orthorhombic metastable form of polymorph II), L-glutamic acid (selective crystallization of forms α and β), and L-histidine (selective crystallization of forms A and B) (Drioli et al. 2012).

When investigating nucleation kinetics, an important parameter is the induction time, defined as the time elapsed from the attainment of a given supersaturation up to the formation of critical nuclei. As a general rule, a higher nucleation rate (lower ΔG^*) results in a shorter induction time. This is particularly evident in the crystallization of proteins: macromolecules display a rather asymmetric and weak bonding configuration at their surfaces and tend to aggregate in n-mers that diversify the shape and size of lattice units, thus making ordered attachment for growing units less probable.

Experiments carried out on various hydro-soluble proteins (such as lysozyme, trypsin, β -glucosydase) showed the possibility to obtain a crystalline product in shorted times with respect to those measured when using conventional vapor diffusion techniques under the same supersaturation level (Curcio et al. 2010). Moreover, X-ray diffraction analysis by synchrotron radiation confirmed a high structural order of crystals grown on microporous membranes (i.e., polypropylene). Crystallization experiments on metals-proteins have also resulted in a new orthorhombic form P21212 of the complex Lysozyme- Co^{2+} .

In order to understand the effect of the chemistry of surface on the heterogeneous nucleation, Curcio et al. (2014) investigated the mechanisms of acetaminophen (ACM) crystal formation due to specific solute-surface interactions on polydimethylsiloxane (PDMS) with siloxane functional groups $\text{Si} - \text{O} - \text{Si}$ forming the backbone of silicones, partially fluorinated elastomer polyvinylidenedifluoride (PVDF), polystyrene (PS) having weak electron-donor phenyl rings, poly(*n*-buthyl methacrylate) (P *pu* BMA) showing ester functionality, polyimide (PI) that includes both hydrogen-bond acceptor imide functionality and carbonyl groups, ethylene/acrylic acid (EAA) copolymer with only the carboxyl moiety. Power X-ray Diffraction analysis showed the occurrence of preferred orientation (PO) depending on the strength of the intermolecular interactions occurring at the polymer-crystal interface during nucleation: from nonspecific adsorption (PDMS, PnBMA, and PS) to oriented arrangement of molecules in the crystalline lattice (EAA, PI, and PVDF) (Curcio et al. 2014).

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Membrane Crystallization in Pharmaceuticals, Application of

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Definition

Controlling polymorphism with membrane-based crystallizers: application to form I and II of paracetamol. Selective glycine polymorph crystallization by using microporous membranes. Effect of supersaturation control and heterogeneous nucleation on porous membrane surfaces in the crystallization of L-glutamic acid polymorphs.

Many substances can exist in solid crystalline state as several phases, a phenomenon named polymorphism. Each polymorph is characterized by its specific physical properties, like solubility, dissolution rate, thermal and mechanical stability, optical properties, etc. Therefore, each form represents a specific material, different to some extent from the other phases of the same substance, and this has remarkable implications for its specific utilization in industrial, technological, and scientific applications. Among the different phases, the relative stability in a specific condition is ruled by thermodynamics, as described by the classical nucleation theory (CNT) (Kashchiev 2001). However, the phase that will be effectively obtained depends on kinetics (Ostwald 1987). This is because a competition between the thermodynamic and kinetic control of the nucleation

phase, in combination with the relative growth rates of the different polymorphs, will affect the final outcome of the crystallization process.

In a membrane crystallizer, this kind of control can be achieved by controlling the composition of the crystallizing solution through the management of the transmembrane flux. This provides an opportunity to systematically affect the rate of variation of the supersaturation which, in turn, affects the polymorphic composition of the precipitate. As this control can be produced very precisely, by fine-tuning the operating conditions and/or by choosing the opportune membrane properties, selective polymorph crystallization is an important possibility available with membrane crystallization technology (Di Profio et al. 2007a). Namely, during a crystallization process, when the least stable structure (or a mixture of nuclei of the different polymorphs) forms following an Ostwald-like behavior, the relative growth rates of the different phases with respect to the supersaturation generation rate will fix which form will effectively be grown. When the rate of variation of supersaturation is low, due to the low evaporation rates through the membrane, if nuclei of the more stable structure have time to grow at the expense of the less stable forms via solvent-mediated transfer of solute, a “thermodynamic control” and the more stable polymorph will selectively (or prevalently) be obtained. However, for higher evaporation rates, the increase in the metastable zone width induces nucleation at higher values of supersaturation. In this situation, the conversion from the metastable to the stable phase could not be fast enough with respect to the growth of the former, so that the growth of the kinetically favored form (metastable), which might be also the first to appear according with the Ostwald rule of stages, is observed. In this case the overall process is “kinetically controlled” (Di Profio et al. 2007b). Accordingly, high control of the membrane-based process provides the possibility to induce polymorphic selection during crystallization by switching between a kinetic and a thermodynamic control of the nucleation stage thus allowing the production of either a metastable or a stable structure (Di Profio et al. 2009).

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Membrane Definition

- [Membrane \(Definition, Function, Structure\)](#)

Membrane Dehumidification of Atmospheric Air

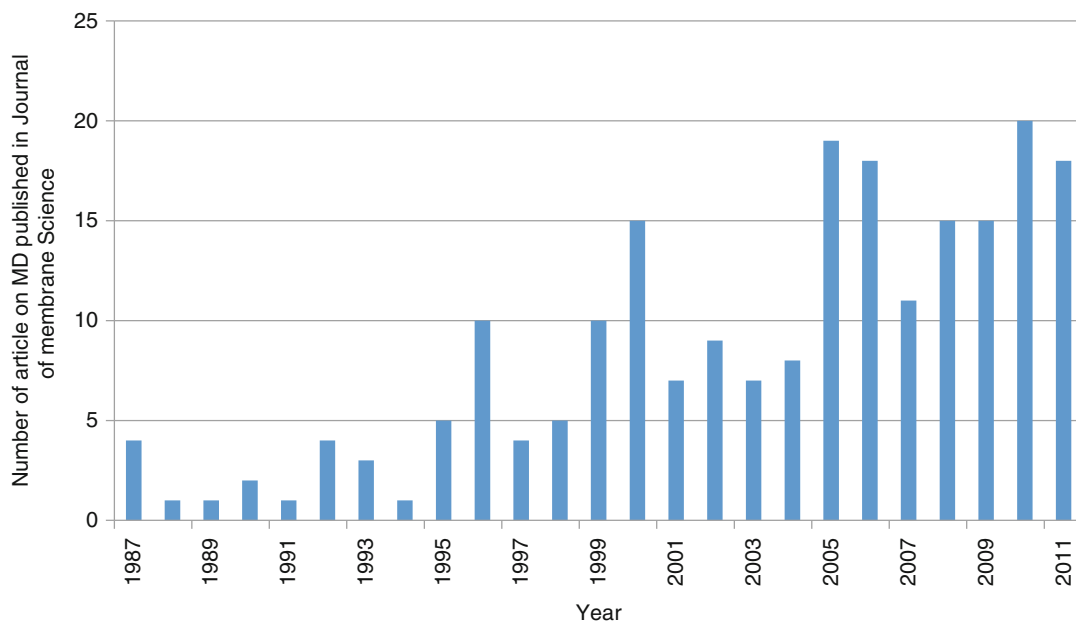
- [Dehumidification of Atmospheric Air by Membrane Technology](#)

Membrane Distillation (MD)

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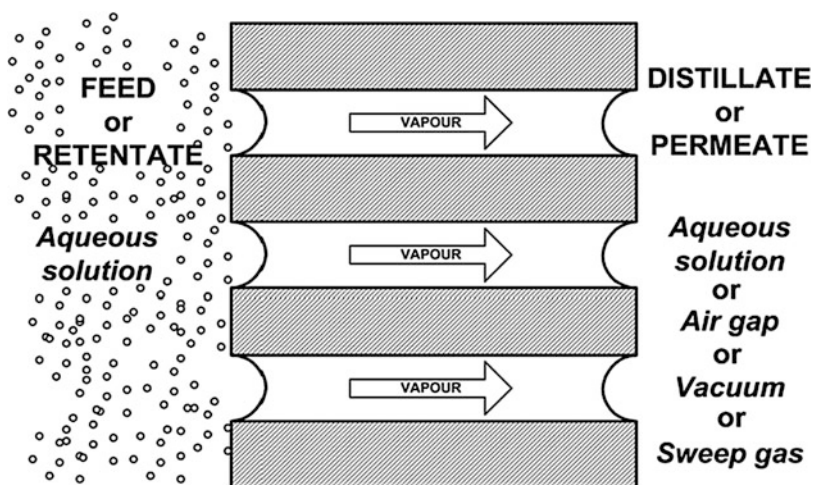
Membrane distillation (MD) is a thermal membrane operation known for more than 50 years (first patent was filed by Bodell on 3 June 1963 (Findley 1967); first MD paper was published 4 years later by Findley (Bodell 1963)). During the last years, the number of papers published on MD and the research groups focusing on MD studies have been increasing (Fig. 1).

MD has great potential as a concentration process at low temperature and energy with respect to



Membrane Distillation (MD), Fig. 1 Number of the papers published in *Journal of Membrane Science* on MD field each year up to September 2011 (Drioli et al. 2012)

Membrane Distillation (MD), Fig. 2 General scheme of the MD process: aqueous solution on feed side whereas four different solutions can be realized on permeate side (aqueous solution or air gap or vacuum or sweeping gas) (Lawson and Lloyd 1997)



M

conventional processes, such as distillation and reverse osmosis (RO). MD allows the separation of volatile components from solutions. If the solutions contain nonvolatile components, it is possible to remove solvent by concentrating the solutions.

In MD, one side (feed side) of a hydrophobic membrane is brought into contact with a heated, aqueous feed solution. The hydrophobic nature of

the membrane prevents penetration of the aqueous solution into the pores, resulting in a vapor–liquid interface at each pore entrance. Here, volatile compounds evaporate, diffuse and/or convect across the pores, and are condensed on the opposite side (permeate) of the system (Fig. 2). The driving force of the process is linked to the vapor-pressure gradient between the two membrane sides.

The documented and expected benefits resulting from MD are as follows:

- The nature of the driving force and the hydro-repellent character of the membrane allow the theoretically complete rejection of nonvolatile components such as macromolecules, colloidal species, and ions.
- Lower temperatures with respect to those usually used in conventional distillation column are sufficient to establish interesting transmembrane flux, with consequent reduction of energy costs, thus allowing the efficient recycle of low-grade waste heat streams as well as the use of alternative energy sources (solar, wind, or geothermal).
- Lower pressures with respect to those usually utilized in RO because the required operating pressures are of the order of few hundred kPa. Lower operating pressure translates to lower equipment costs, increased process safety, and possibility of using plastic equipment, thus reducing or avoiding erosion problems.
- If compared to RO process, MD permeate flux is only slightly affected by the concentration of the feedwater, and thus, productivity and performance remain roughly the same for high concentration feedwaters. This means that MD can be preferentially employed whenever elevated permeate recovery factors or high retentate concentrations are requested. On the contrary, in MD temperature polarization, similar to concentration polarization, arises from heat transfer through the membrane and it is often the rate-limiting step for mass transfer.
- Since MD membranes act merely as a support for a vapor–liquid interface, they do not distinguish between solution components on a chemical basis, do not act as a sieve, and do not react electrochemically with the solution; they can be fabricated from almost any chemically resistant polymers with hydrophobic intrinsic properties, such as polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidene difluoride (PVDF). This characteristic increases membrane life. New amorphous perfluoro polymers (e.g., Hyflon, Teflon) can be also utilized neglecting their

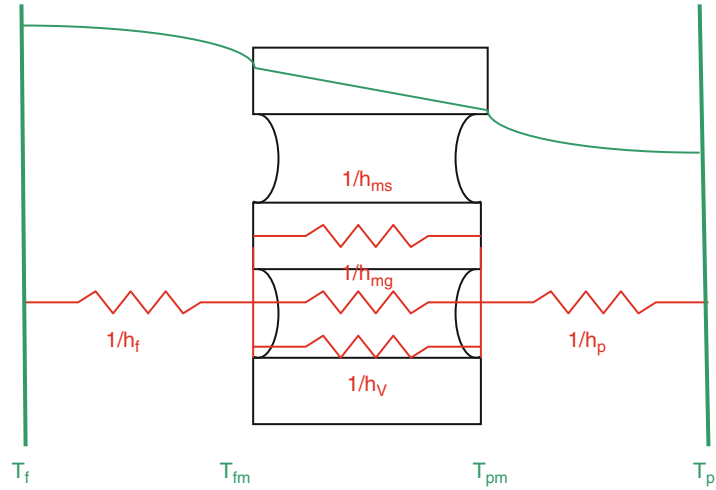
still high costs. On the other hand, MD performance (in particular the transmembrane flux and the heat loss by conduction through the membrane) is intrinsically affected by the structure of the membrane in terms of thickness, porosity, mean pore size, pore distribution, and geometry.

- Membrane fouling is less problematic in MD than in other membrane separations because (i) the pores are relatively large compared to RO/UF pores; (ii) the process liquid cannot wet the membrane – therefore, fouling layers can be deposited only on the membrane surface but not in the membrane pores; and (iii) due to the low operating pressure of the process, the deposition of aggregates on the membrane surface would be less compact and only slightly affect the transport resistance.
- On the contrary, one problem that can arise in MD is the *membrane wetting* which occurs when the liquid penetrates into the membrane pores. Once a pore has been penetrated, it is said to be “wetted” and the membrane must be completely dried and cleaned before the wetted pores can once again support a vapor–liquid interface.

In MD process both heat and mass transfer phenomena occur through the membrane. Figure 3 illustrates the possible heat transfer resistances in MD with an electrical analogy.

Heat is first transferred from the heated feed solution of uniform temperature T_f , across the thermal boundary layer to the membrane surface at a rate $Q = h_f \cdot \Delta T_f$. At the surface of the membrane, liquid is vaporized and heat is transferred across the membrane at a rate $Q_v = h_v \cdot \Delta T_m = N \cdot \Delta H_v$ (where N is the rate of mass transfer and ΔH_v is the heat of vaporization). Additionally, heat is conducted through the membrane material and the vapor that fills the pores at a rate $Q_m = h_m \cdot \Delta T_m$ where $h_m = \varepsilon \cdot h_{mg} + (1 - \varepsilon)h_{ms}$ (ε is the membrane porosity; h_{mg} and h_{ms} represent the heat transfer coefficients of the vapor within the membrane pores and the solid membrane material, respectively). Conduction is considered a heat loss mechanism because no corresponding mass transfer takes place. Total heat transfer

Membrane Distillation (MD), Fig. 3 Heat transfer resistances in MD



across the membrane is $Q = Q_v + Q_m$. Finally, as vapor condenses at the vapor–liquid interface, heat is removed from the cold-side membrane surface through the thermal boundary layer at a rate $Q = h_p \cdot \Delta T_p$.

The overall heat transfer coefficient of the MD process is given by

$$\frac{1}{U} = \frac{1}{h_f} + \frac{1}{h_m + h_v} + \frac{1}{h_p} = \frac{1}{h_f} + \frac{1}{\left(\frac{K_g \cdot \varepsilon + K_m(1 - \varepsilon)}{\delta}\right) + \left(\frac{N \cdot \Delta H_v}{T_{fm} - T_{pm}}\right)} + \frac{1}{h_p} \quad (1)$$

where each h and each T represent the corresponding heat transfer coefficients and temperatures shown in Fig. 3.

The total heat transferred across the membrane is given by

$$Q = U \cdot \Delta T \quad (2)$$

Equation 1 illustrates the importance of minimizing the boundary layer resistances (maximizing the boundary layer heat transfer coefficients). A commonly used measure of the magnitudes of the boundary layer resistances relative to the total heat transfer resistance of the system is given by the temperature polarization coefficient (TPC):

$$TPC = \frac{T_{fm} - T_{pm}}{T_f - T_p} \quad (3)$$

- If $TPC \rightarrow 1$, the MD system is well designed, and it is limited by mass transfer.
- If $TPC \rightarrow 0$, the MD system is poorly designed and it is limited by heat transfer through the boundary layers.

In literature, the recommended range of TPC is from 0.4 to 0.7 for well-designed systems (Lawson and Lloyd 1997).

The boundary layer heat transfer coefficients are almost always estimated from empirical correlations such as the following:

- Sieder–Tate correlation for turbulent liquid flow inside circular tubes

$$h = \frac{Nu \cdot K^T}{d}, \quad Nu = 0.023 \cdot Re^{0.8} \cdot Pr^{1/3}.$$

$$\phi_\mu^{0.14} \text{ or } \frac{hd}{K^T} = 0.023 \cdot \left(\frac{dG}{\mu}\right)^{0.8} \cdot \left(\frac{c_p \mu}{K^T}\right)^{1/3} \cdot \left(\frac{\mu}{\mu_w}\right)^{0.14} \quad (4)$$

where d is the tube diameter, K^T is the thermal conductivity of the liquid, G is the mass velocity equal to $w/S = \langle \rho v \rangle$, μ is the bulk liquid viscosity, μ_w is the liquid viscosity at the wall, c_p is

the liquid heat capacity, and ϕ_μ is the heating/cooling correction factor.

Equation 4 should be used for $Re > 6000$ and for tubes with large ratios L/d (where L is the tube length). For short tubes ($L/d < 50$), several corrections are available, including $\frac{h}{h_\infty} = 1 + \left(\frac{d}{L}\right)^{0.7}$

where h_∞ is the heat transfer coefficient given by Eq. 4.

For the case of a noncircular flow channel, these correlations can still be used if the equivalent diameter d_e of the flow channel is substituted:

$$d_e = 4 \cdot r_H = 4 \cdot \frac{S}{L_p} = 4 \cdot \frac{\text{cross-sectional area of the flow channel}}{\text{length of the wetted perimeter of the flow channel}} \quad (r_H = \text{hydraulic radius})$$

- Sarti correlation for laminar liquid flow in circular tubes with constant wall temperature:

$$Nu = 3.66 + \frac{0.067 \cdot Gz}{1 + 0.04 \cdot Gz^{2/3}} \quad \text{where}$$

$$Gz = \frac{\dot{m} c_p}{K^T L} \quad (5)$$

where G_z is the Graetz number, $\dot{m}$ is the mass flow rate, c_p is the liquid heat capacity, K^T is the liquid thermal conductivity, and L is the length of the tubes.

However, several empirical correlations exist which allow to estimate the boundary layer heat

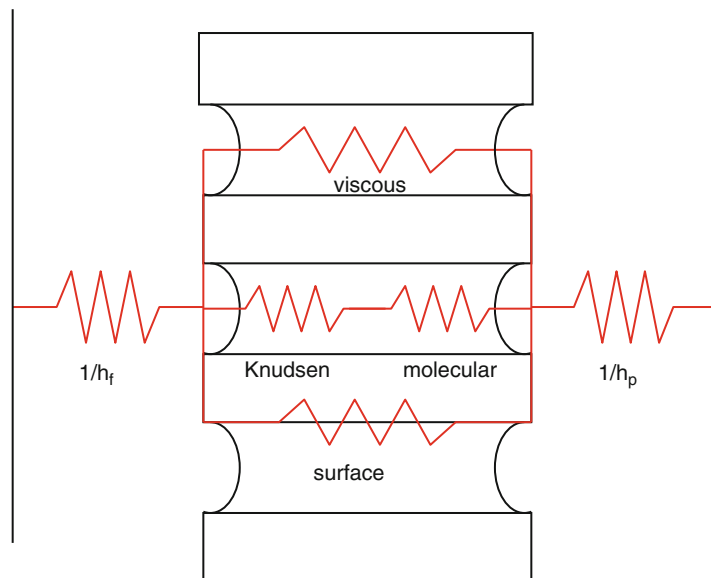
transfer coefficients for other geometries and heat transfer mechanisms.

The heat transfer across the membrane has been already described. For what concerns the heat transferred by convection within the membrane pores, this can be also considered but is negligible because convection accounts for, at most, 6 % of the total heat lost through the membrane and only 0.6 % of the total heat transferred across the membrane (Lawson and Lloyd 1997).

Regarding mass transfer, Fig. 4 illustrates the possible mass transfer resistances in MD using an electrical analogy.

The resistances shown in Fig. 4 are arranged as described by the dusty gas model (DGM), which

Membrane Distillation (MD), Fig. 4 Mass transfer resistances in MD



is a general model for mass transport in porous media.

- *Mass transfer across boundary layers*

A mass balance across the feed side boundary layer yields the relationship between molar flux N , the mass transfer coefficient k_x , and the solute concentrations c_m and c_b at the interface and in the bulk, respectively (Curcio and Drioli 2005; Mya Tun et al. 2005):

$$\frac{N}{\rho} = k_x \ln \frac{c_m}{c_b} \quad (6)$$

where ρ is the solution density.

The method that is used in literature to determine the mass transfer coefficient is to employ an analogy between heat and mass transfer. Therefore, Eqs. 4 and 5 can be used to estimate boundary layer mass transfer coefficients by substituting the Sherwood number for the Nusselt number, the Schmidt for the Prandtl, and the mass transfer Graetz number for its heat transfer form. In general, the used correlations are as follows:

$$Sh = \alpha Re^\beta Sc^\gamma \quad (7)$$

where Sh = Sherwood number = $(k_x d_h)/D$ (d_h hydraulic diameter, D diffusion coefficient in the liquid), Sc = Schmidt number = $\mu/(\rho D)$ (μ is the bulk liquid viscosity; ρ is the solution density), and Gz_M = mass transfer Graetz number = $Gz_M = \frac{\dot{m}}{\rho D_{AB} L}$ ($\dot{m}$ is the mass flow rate; L is the tube length).

As a result of the solvent transmembrane flux across the membrane, when aqueous solutions containing nonvolatile solutes are considered, the concentration of the nonvolatile solutes at the membrane surface (C_{Bm}) becomes higher than that at the bulk feed (C_{Bb}) with time as long as the separation process is taking place. Almost 100 % of separation is obtained. In this case, care must be taken as supersaturation states may eventually be achieved affecting the efficiency of the membrane process. The term concentration polarization coefficient (CPC) is defined to quantify the mass transport resistance

within the concentration boundary layer at the feed side as follows:

$$CPC = \frac{C_{Bm}}{C_{Bb}} \quad (8)$$

The increased concentration of nonvolatile compounds next to the membrane surface would have the influence of reducing the transmembrane flux due to the establishment of concentration polarization (CP) layer at the feed side that acts as a mass transfer resistance to the volatile molecule species (water). Fortunately, in MD process, the low to moderate flow rates and high heat transfer coefficients reduce the impact of concentration polarization, which is lower than that of the temperature polarization effect (Laganà et al. 2000; El-Bourawi et al. 2006; Drioli et al. 1999; Srisurichan et al. 2006). In fact, boundary layers next to the membrane can contribute substantially to the overall transfer resistance; heat transfer across the boundary layers is often the rate-limiting step for mass transfer in MD because a large quantity of heat must be supplied to the membrane surface to vaporize the liquid and because the membrane fabrication technology has improved in the last decades so much that MD process has shifted away from being limited by mass transfer across the membrane to being limited by heat transfer through the boundary layers on either side of the membrane.

- *Mass transport through the membrane pores*

As stated earlier, the mass transfer process in MD is driven by the imposed vapor-pressure gradient between both sides of the membrane. The mass transport mechanism is governed by three basic mechanisms known as Knudsen diffusion, Poiseuille flow, and molecular diffusion or the combinations between them known as transition mechanism (excluding surface diffusion, negligible in MD because, by definition of the MD phenomenon, molecule—membrane interaction is low and the surface diffusion area in MD membranes is small compared to the pore area).

The dusty gas model is usually used as a general model taking into account the latter basic mechanisms (Lawson and Lloyd 1997; Curcio and Drioli 2005; El-Bourawi et al. 2006):

$$\frac{N_i^D}{D_{ie}^k} + \sum_{j=1 \neq i}^n \frac{p_j N_i^D - p_i N_j^D}{D_{ije}^0} = \frac{-1}{RT} \nabla p_i \quad (9)$$

$$N_i^V = -\frac{\varepsilon r^2 p_i}{8 R T \tau \mu} \nabla P \quad (10)$$

$$D_{ie}^k = \frac{2 \varepsilon r}{3 \tau} \sqrt{\frac{8 R T}{\pi M_i}} \quad (11)$$

$$D_{ije}^0 = \frac{\varepsilon}{\tau} D_{ij}^0 \quad (12)$$

where N^D is the diffusive flux, N^V is the viscous flux, D^k is Knudsen diffusion coefficient, D^0 is the ordinary diffusion coefficient, p_i is the partial pressure of the component i , P is the total pressure, M_i is the molecular weight of component i , r is the membrane pore radius, ε is the membrane porosity (assuming the membrane consists of uniform cylindrical pores), μ is the fluid viscosity, and τ is the membrane tortuosity. The subscript “e” is indicative of the effective diffusion coefficient function of the membrane structure.

There is only one problem with the application of the DGM to MD, and that lies in the fact that MD is a non-isothermal process. The DGM was derived for isothermal flux, but has been successfully applied to non-isothermal systems via the inclusion of terms for thermal diffusion and thermal transpiration. However, it is easily shown (Lawson and Lloyd 1997) that these terms are negligible in the MD operating regime, and T_{avg} in the membrane is used in place of T in the DGM equations.

Regardless of which mechanism is involved in the mass transportation process, the molar flux, N , must be proportional to the vapor-pressure difference across the membrane:

$$N = C \cdot \Delta P$$

where ΔP is the vapor-pressure difference across the membrane (function of temperatures and compositions at the membrane surface) and C is the membrane distillation coefficient that can be obtained experimentally. C is a function of temperature, pressure, and composition within the membrane as well as membrane structure and depends on the MD configuration employed as well as on the Knudsen number (Kn , ratio of the mean free path of the transported gas molecules (λ) through the membrane pores to the mean pore diameter of the membrane (d)). In fact, Kn number determines the physical nature of flow through membrane pores, and since the membranes used in MD exhibit pore size distribution, more than one mechanism may occur through the membrane.

Whereas on feed side only an aqueous solution can be present, the nature of the permeate can be different and gives origin to the four basic MD configurations:

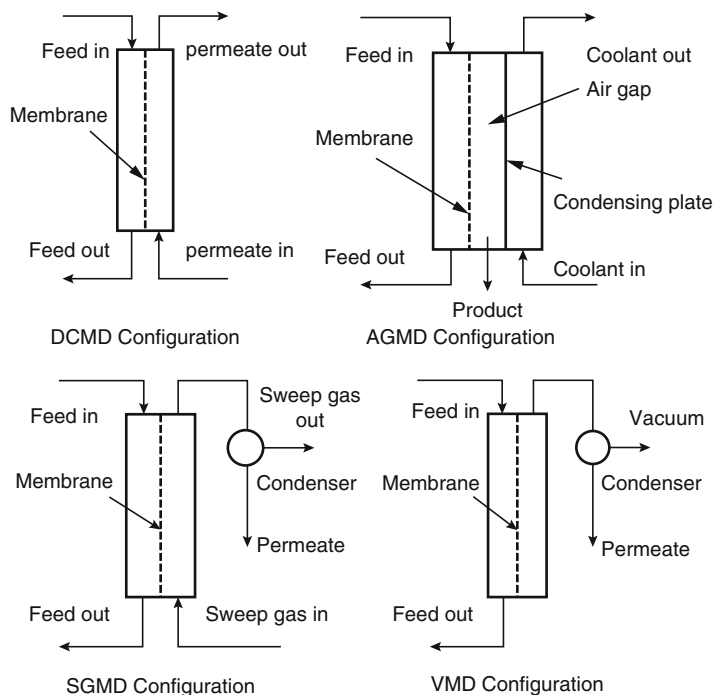
- Direct contact MD (DCMD), in which the permeate is in liquid phase and, therefore, the membrane is on both sides *directly* in contact with aqueous solutions
- Vacuum MD (VMD), in which the vaporized solvent is recovered by vacuum and condensed, if needed, in a separate device
- Air gap MD (AGMD), in which an air gap is interposed between the membrane and a condensation surface
- Sweeping gas MD (SGMD), in which a stripping gas is used as a carrier for the removal of the produced vapor (Fig. 5)

The type of employed MD depends upon permeate composition, flux, and volatility:

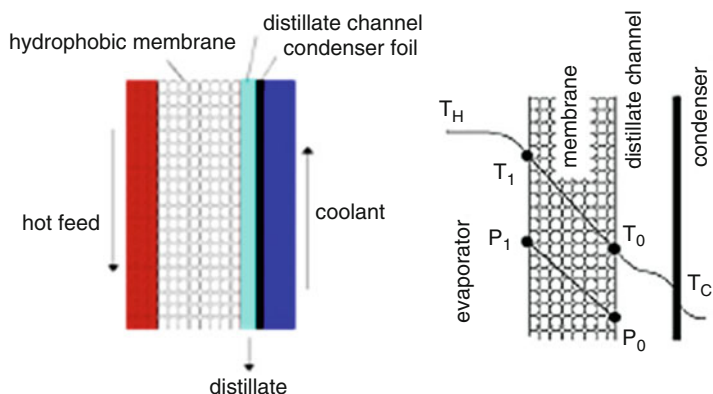
- SGMD and VMD are typically used to remove volatile organic or dissolved gas from an aqueous solution.
- Because AGMD and DCMD do not need an external condenser, they are best suited for applications where water is the permeating flux.
- The DCMD configuration, which requires the least equipment and is simplest to operate, is

Membrane Distillation

(MD), Fig. 5 Common configurations of the membrane distillation process that may be utilized to establish the required driving force (El-Bourawi et al. 2006)

**Membrane Distillation**

(MD), Fig. 6 Basic channel arrangement and temperature profile for PGMD (Winter et al. 2011)



best suited for applications such as desalination or the concentration of aqueous solutions (orange juice), in which water is the major permeate component.

- AGMD, which is the most versatile MD configuration, can be applied to almost any applications.

Some new configurations with improved energy efficiency, better permeation flux, or smaller footprint have been proposed such as material gap

membrane distillation, multi-effect membrane distillation, multi-effect vacuum membrane distillation, permeate gap membrane distillation, and hollow fiber multi-effect membrane distillation.

Permeate gap membrane distillation (PGMD) is an enhancement of DCMD in which a third channel is introduced by an additional non-permeable foil (Fig. 6).

One significant advantage of PGMD is the separation of the distillate from the coolant. Therefore the coolant can be any other liquid,

such as cold feedwater. This offers the opportunity to integrate an efficient heat recovery system.

Multi-effect membrane distillation (MEMD) is based on the concepts of multi-stage and multi-effect distillation for seawater desalination. The cold feed solution is placed beneath the condensation surface as a coolant to condense the permeated vapors as well as to gain heat at the same time. The pre-heated feed solution is further heated before it enters the feed channel.

Vacuum-multi-effect membrane distillation (V-MEMD) is a modified form of VMD that integrates the concept of multi-effect distillation into the VMD. As a general principle of the process, the vapors produced in each stage are condensed during the subsequent stages. Vapors are generated in steam raiser working under vacuum by exchanging the heat provided by external source. The vapors are introduced in first stage where these are condensed by exchanging the heat with feed via a foil. The vapors generated in first stage are transported through the membrane and collected on the foil in the second stage. It has been claimed that these modules have excellent gained to output ratio which is crucial parameter for industrial applications (Zhao et al. 2013). A condenser is used to condense the vapors generated in final stage. The vapor pressure in each stage is less than its preceding stage.

Material gap membrane distillation (MGMD) consists of filling the gap between the membrane and the condensation plate with different materials having different characteristics such as polyurethane (sponge), polypropylene mesh, sand, and deionized water in order to increase transmembrane flux with respect to AGMD.

Osmotic distillation (OD) represents another extension of the MD concept: a microporous hydrophobic membrane separates two aqueous solutions that are kept in contact at different solute concentrations; this difference in activity causes a vapor-pressure difference that activates mass transport through the membrane. Because OD operates essentially at room temperature, it is appropriate for applications in the agro-food industry (such as in integrated membrane system for the clarification and the concentration of citrus and carrot juices that has been proposed as an

alternative and efficient approach to the traditional techniques currently in operation), in pharmaceutical biotechnology, and medicine (more information can be found in Drioli et al. (2006), Drioli et al. (2015)).

To date, the slow progress of MD has been related with the unavailability of appropriate membranes and modules for MD applications, high energy consumption with respect to RO that increases the overall energy demand, membrane wetting, and low flux. However, thanks to the recent and growing extensive research activities carried out in various areas of MD, the process has become much more attractive due to the availability of better membranes and to the possibility to utilize alternative energy sources in niche applications.

Cross-References

► Alcohol Removal by Membrane Operations

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Membrane Distillation Applications

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Membrane distillation (MD) is a non-isothermal process that allows the separation of volatile components from solutions. If the solutions contain nonvolatile components, it is possible to remove solvent by concentrating the solutions. MD has been applied for separation of nonvolatile components from water like ions, colloids, and macromolecules (El-Bourawi et al. 2006; Lawson and Lloyd 1996, 1997; Mengual and Pena 1997; Khayet et al. 2003, 2006; Sudoh et al. 1997; Drioli et al. 1986; Zolotarev et al. 1994); for the removal of trace volatile organic compounds from water such as benzene, chloroform, and trichloroethylene (Lawson and Lloyd 1997; Duan et al. 2001; Banat and Simandl 1996, 2000; Sarti et al. 1993; Qureshi et al. 1994; Banat and Al-Shannag 2000); or for the extraction of other organic compounds such as alcohols from dilute aqueous solutions (Lawson and Lloyd 1997; Garcia-Payo et al. 2000; Banat and Simandl 1999; Bandini et al. 1997; Bandini and Sarti 1999). As a

consequence, MD is suited for both concentration of aqueous solutions and water production. In fact, MD has been applied for water desalination where near 100 % rejection of nonvolatile ionic solutes is easily achieved (an example can be found in the European-funded project MEDINA (Drioli et al. 2011)), wastewater treatment and food processing (concentration of juice and raw cane sugar), and biomedical applications (such as water removal from blood and treatment of protein solutions) (El-Bourawi et al. 2006). Moreover, thanks to its characteristic to work at lower temperatures with respect to those usually used in thermal processes and thus allowing the efficient use of alternative energy sources (solar, wind, or geothermal), MD has been considered a valid desalination operation in arid areas with abundant solar energy available.

However, a lot of other interesting applications of MD have been explored due to less fouling tendency of the process and the potential to treat complex feed solutions. Separation of azeotropic aqueous mixtures such as alcohol–water mixtures, concentration of radioactive solutions and application for nuclear desalination, wastewater treatment in which a less hazardous waste can be discharged to the environment specially in textile waste treatment that is contaminated with dyes, concentration of coolant (glycol) aqueous solutions, treatment of humic acid solutions, pharmaceutical wastewater treatment, and in areas where high-temperature applications lead to degradation of process fluids can be attractive (Banat and Simandl 1996).

In addition, due to the chemical stability of the employed membranes, MD can also be applied for the concentration of acids (Tomaszewska 1993; Tomaszewska et al. 1995; Tang et al. 2003). A list of innovative and potential uses of MD for various applications mentioned in the recent literature is provided in Table 1.

More recently membrane distillation has been also used in membrane bioreactor configuration (MDBR) for the treatment of industrial and municipal used waters, in order to retain effectively small size and persistent contaminants (Phattaranawik et al. 2008). The possibility to combine MD with the production of high-quality

Membrane Distillation Applications, Table 1 Applications of MD mentioned in different recent studies (Reprinted with permission from Drioli et al. 2015, Elsevier)

Feed	Target	Used membranes	MD configuration	References
Seawater	Boron removal	PVDF	DCMD	Hou et al. (2013)
Simulated water	Chromium removal	PTFE	DCMD	Bhattacharya et al. (2014)
Produced water	Desalination	PTFE	DCMD	Singh and Sirkar (2012)
Aqueous solution of <i>N</i> -methyl-2-pyrrolidone	Concentration of <i>N</i> -methyl-2-pyrrolidone solution	PP	VMD	Shao et al. (2014)
Cooling tower blow-down water	Desalination	FS PP	DCMD	Yu et al. (2013)
Aqueous ammonia solution	Removal of ammonia	PVDF capillary	DCMD and MDCMD	Qu et al. (2013)
Olive oil waste mill water	Concentration of phenolic compounds	FS PTFE	DCMD	Xie et al. (2013)
Produced water	Desalination	FS PTFE	AGMD	Alkhudhiri et al. (2013)
Model lactose solution	Ethanol production	PP capillary membrane	DCMD	Tomaszewska and Białończyk (2013)
Synthetic solution of trace OC	Removal of complex trace organic compounds	FS PTFE	DCMD	Wijekoon et al. (2014)
Aqueous H ₂ SO ₄ solution	Concentration of H ₂ SO ₄ solution	PP hollow fiber	Multi-effect MD	Li et al. (2012)
Retentate of NF and RO	Improvement of water RF and salt crystallization	PVDF hollow fibers	DCMD	Tun and Groth (2011)
Water from Great Salt Lake	Recovery of minerals	FS PTFE and PP	DCMD	Hickenbottom and Cath (2014)
Zabłocka Thermal Brine	Brine concentration	PP hollow fiber accrual	DCMD	Gryta (2013)
Glycerol fermentation broth	Separation of acetic acid from the broth	Accurel PP hollow fiber	DCMD	Gryta et al. (2013)
Synthetic radioactive wastewater	Removal of radioactive elements	Hydrophobically modified FS PS or PES	DCMD	Khayet (2013)
Wastewater containing arsenic in different concentrations	Removal of arsenic	PP and PVDF FS	VMD	Criscuoli et al. (2013)

crystals extracted from the brine of nanofiltration (NF) and reverse osmosis (RO) is particularly interesting and promising as suggested in Drioli et al. (2011), Macedonio et al. (2007), and Macedonio and Drioli (2010). Moreover, membrane distillation can be also utilized in integrated system with pressure retarded osmosis (PRO) or reverse electrodialysis (RED) for utilizing salinity gradient for energy production (the so-called blue

energy). An example can be found in the Megaton project (Kurihara and Hanakawa 2013) in Japan and in the SeaHero project (Kim et al. 2009, 2011) in South Korea. In the last part of these two projects, hybrid systems with MD and PRO units have been proposed for the extraction of valuable resources from the brine, the minimization of the environmental impact of the brine, and the recovery of energy.

List of Symbols

AGMD Air gap membrane distillation
DCMD Direct contact membrane distillation
FS PP Flat sheet polypropylene
FS PS or PES Flat sheet polysulfone or polyethersulfone
FS PTEF Flat sheet polytetrafluoroethylene
MDCMD Modified direct contact membrane distillation
PP and PVDF FS Polypropylene and polyvinylidene difluoride flat sheet
PP Polypropylene
PTFE Polytetrafluoroethylene
PVDF Polyvinylidene difluoride
VMD Vacuum membrane distillation

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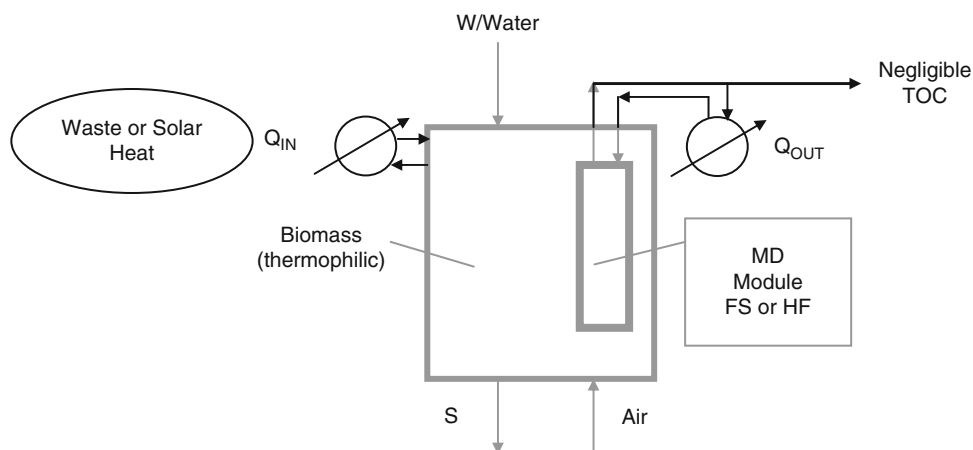
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Membrane Distillation Bioreactor (MDBR)

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The Membrane Distillation Bioreactor (MDBR) combines a wastewater bioreactor with membrane distillation (MD) (Fane et al. 2012). It is shown schematically in Fig. 1. The MDBR is a member of the Membrane Bioreactor (MBR) family but with important differences from the conventional MBR. The conventional MBR uses microporous membranes, either microfiltration (MF) or ultrafiltration (UF), to retain biomass, or mixed liquor, within the reactor. The MDBR employs a MD membrane to retain the mixed liquor and provide the treated wastewater. The MDBR membranes can be either submerged in the bioreactor or located in a sidestream. An elevated temperature, typically 50–60 °C, is used to drive water across the membrane and this means that thermophilic biomass are required. In addition the hydrophobic membrane retains nonvolatile salts that accumulate in the reactor. Therefore the MDBR biomass need to be salt tolerant (halotolerant). The MDBR concept provides a “high retention” MBR, wherein low molecular weight molecules do not leave the reactor through the membrane, as they would through MF or UF membranes in the conventional MBR. This means that the organic retention time (ORT) in the MDBR can be significantly longer than the hydraulic retention time



Membrane Distillation Bioreactor (MDBR), Fig. 1 Membrane distillation bioreactor

(HRT) and recalcitrant organics are given longer to degrade. In contrast the conventional MBR has ORT equal to HRT. The MDBR, in common with other MBRs, typically has a small “bleed”, or wastage, stream to maintain a steady-state concentration of mixed liquor suspended solids (MLSS). The proportion wasted daily determines the “sludge retention time” (SRT); for example 5 % removal per day gives SRT of 20 days, 10 % removal gives SRT of 10 days etc. The accumulation of nonvolatile and nonbiodegradable species in the reactor is determined by the ratio of SRT/HRT, which represents the concentration factor and could exceed 20x. Retained salts can reach significant levels, but with acclimatization the biomass can cope.

The MDBR can provide a high-quality treated water, suitable for reuse. This is due to the unique separation properties of the typical MD membrane. In common with other membrane processes, the MDBR can experience fouling, and this can be controlled by bubbling and occasional cleaning. Experience indicates that the fouling is usually a combination of inorganic scale (calcium salts) and biofouling. Fluxes of the order of 10 l/m²h can be sustained.

The MDBR is a developmental concept and not widely used. However it has been demonstrated in the petrochemical industry (Khaing et al. 2010) providing a highly treated water, and driven by waste heat. Other target industries include food and pharmaceutical wastewaters.

Another opportunity could be water reclamation where an analysis shows a 30 % lower electrical energy usage than a combined MBR and RO process. Recently the MDBR has been operated under anaerobic conditions with the generation of biogas.

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Membrane Distributor

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Synonyms

Distributor Reactor

A membrane distributor is a special type of a membrane reactor with “distributed” feeding,

i.e., one or several reactants are fed through a membrane to the reaction zone (Dittmeyer and Caro 2008; Caro 2010). In general, a selectivity increase can be expected. On the one hand, a more uniform concentration of the dosed reactants can be expected. On the other hand, also a nonuniform but specific shape of a concentration profile can be realized which can be beneficial for kinetic reasons. Further, the total amount of reactants that can be supplied without exceeding the threshold for safe operation can also be increased. One additional effect observed when applying a distributed feed along the reactor is an increasing flow rate downstream which shortens the contact time on catalytic sites.

The concept of “membrane distributor reactor” does not necessarily require a selective membrane, provided that the transmembrane flux can be properly controlled by the differential pressure. Therefore, the distributed feeding can be either (i) selective or (ii) nonselective:

- (i) **Selective supply:** There are numerous examples for the selective feed supply. Examples are the hydrogen supply through a hydrogen-selective membrane (Pd, zeolite, MOF, carbon, etc.) in partial hydrogenations or the oxygen supply through an oxygen-selective membrane (perovskite, other oxygen-transporting ceramics) in partial hydrocarbon oxidations. In both cases, improved selectivities can be expected since the hydrogenations or oxidations take place at constant and low hydrogen/oxygen partial pressure in, e.g., axial direction of a tubular membrane reactor.
- (ii) **Nonselective supply:** In the strong sense of a membrane reactor, only the selective feeding fulfills the definition of a membrane reactor as a device combining membrane-based separation and a chemical reaction in one unit (Koros et al. 1996). However, also in this case, the transmembrane flux can be tuned by the pressure difference, thus controlling the partial pressure of the reactants resulting in a higher selectivity. As an example, porous membranes can be used to distribute oxygen or air in a nonselective manner to the reactor providing a low and uniform oxygen partial

pressure along the reactor. This avoids large differences in the reaction rate and selectivity along the reactor. The use of porous membranes as air distributor is usually not combined with an oxygen enrichment.

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Membrane Dryer

Alessandra Criscuoli

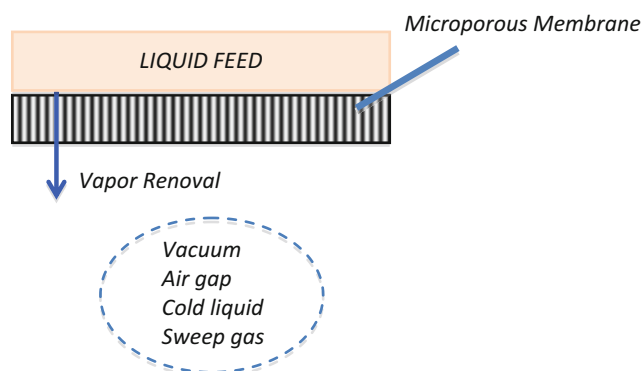
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Membrane Dryer is a membrane-based system able to dry solid particles contained in liquid streams while producing a particle-free liquid (Drioli et al. 2014, Criscuoli et al. 2016). The main principles are those of membrane distillation: the liquid stream (feed) to be treated is in contact with one side of a microporous membrane and the liquid permeates as vapor, thanks to a driving force that can be established across the membrane in different ways: by applying vacuum, by creating an air gap, or by sending a cold liquid or a sweep gas (Fig. 1).

Membranes to be used must be:

1. Microporous;
2. Hydrophobic (for aqueous feeds);
3. Hydrophilic (for organic feeds);
4. With a pore size smaller than the solid particle size.

Membrane Dryer,
Fig. 1 Scheme of a
 membrane dryer



Main advantages with respect to conventional drying systems are:

1. The ability to work with feeds of different concentration (dilute or concentrated feeds)
2. The ability to work with feeds containing solid particles of different size
3. The production of particle-free liquid without the need of a separation step downstream
4. The modularity, flexibility, easy scale-up and scale-down, and low footprint (all typical advantages of membrane processes)

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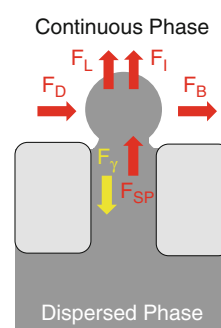
Membrane Emulsification

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Membrane emulsification is a drop-by-drop emulsification method in which the dispersed phase

Membrane Emulsification,
Fig. 1 Droplet formation
 and forces acting at the
 membrane pore level



(as a pure liquid or an emulsion) is pressed through microporous membranes to form droplets at the membrane surface pore level which are collected in the continuous phase (Fig. 1).

The forces acting on a droplet at the membrane pore level include: (i) detaching forces, driving droplets off the pore, and (ii) retaining forces, holding droplets on the pore (Fig. 1, Table 1; Giorno et al. 2009).

The drag force (F_D) is created by the continuous phase flowing parallel to the membrane surface; the buoyancy force (F_{BG}) is due to the density difference between the continuous phase and the dispersed phase; the inertial force (F_I) is caused by the dispersed phase flow moving out from the pore outlet; the dynamic lift force (F_L) results from the asymmetric velocity profile of the continuous phase near the droplet; static pressure (F_{SP}) force is due to the pressure difference between the dispersed phase and the continuous phase at the membrane surface; the interfacial tension force (F_γ) is provided by the effects of dispersed phase adhesion around the edge of the

Membrane Emulsification, Table 1 The forces acting on a droplet at the membrane pore level

Detaching forces		Retaining forces	
Drag force	$F_d = \frac{3}{2} k_x \pi \tau_{c,s} d_d^2$	Interfacial tension	$F_\gamma = \pi d_p \gamma$
Buoyancy force	$F_B = \frac{1}{6} \pi g \Delta \rho d_d^3$		
Lift force	$F_L = 0.761 \frac{\tau_{c,s}^{1.5} \rho_c^{0.5}}{\mu_c} d_d^3$		
Static pressure	$F_{sp} = \frac{\gamma}{d_p} \pi d_d^2$		
Inertial force	$F_I = \rho_d \left(\frac{d_d}{\varepsilon} \right) A_N$		

d_d droplet diameter, A_N cross-sectional area of the droplet neck, k_x equal to 1.7 and takes into account the wall correction factor for a single sphere touching an impermeable wall, ε membrane porosity, $\tau_{c,s}$ wall shear stress, γ dynamic interfacial tension, ρ_c density of the continuous phase, ρ_d density of the dispersed phase, μ_c viscosity of the continuous phase, $\Delta \rho$ the difference between continuous and dispersed phase density

pore opening. In the case of “moving membrane” emulsification, additional forces have to be considered. For rotating membrane emulsification, the additional forces are the centrifugal force to aid droplet detachment and the tangential velocity differences between the droplet and the continuous phase. For an oscillating membrane system where the membrane is transversally excited, an additional drag force and an inertial force appear in the direction parallel to the membrane.

The influence of different parameters on particle diameter (D_p), particle size distribution (PSD), and process productivity (volumetric flux of the disperse phase normalized by the actual membrane area and time (J_d)) is summarized in Table 2.

Table 2 demonstrates that:

Particle size is significantly influenced by:

- *The pore size of the membrane.* The particle size increases linearly with the membrane pore size (Katoh et al. 1996).
- *The surface wetting properties of the membrane.* Membranes unwetted by the dispersed phase allow the generation of droplets with particle size controlled by the membrane pore size. On the contrary, the spread of the dispersed phase on the membrane as a consequence of the wettability determines the uncontrolled production of the droplets (Piacentini et al. 2014).
- *The wall shear stress.* The particle size becomes smaller as the wall shear stress increases and the influence is greater for low wall shear stresses and more effective

Membrane Emulsification, Table 2 The influence of different parameters on particle diameter (D_p), particle size distribution (PSD), and process productivity (J_d)

Parameters	D_p	PSD	J_d
Membrane parameters			
Pore size	☆☆☆	☆	☆☆☆
Pore size distribution	☆☆	☆☆☆	☆
Pore border morphology	☆☆	☆	☆☆
Number of active pores	☆☆	☆	☆☆☆
Distance between pores	☆☆	☆☆☆	☆
Porosity	☆☆	☆☆☆	☆☆☆
Surface wetting property	☆☆☆	☆☆	☆☆☆
Process parameters			
Wall shear stress	☆☆☆	☆☆☆	☆
Transmembrane pressure	☆☆	☆☆	☆☆☆
Temperature	☆	☆	☆☆
Phase parameters			
Emulsifier type and concentration	☆☆☆	☆☆	☆
Viscosity of dispersed phase	☆☆	☆	☆☆☆
Viscosity of continuous phase	☆☆	☆	☆

☆☆☆ very significant; ☆☆ significant; ☆ not significant

for smaller membrane pores size (Katoh et al. 1996).

- *The emulsifier type and concentration.* The faster emulsifier molecules adsorbed at newly formed interfaces, the smaller the emulsion droplets due to the influence of emulsifier on the interfacial tension. Particle size decreased as a function of emulsifier concentration as the interfacial tension had decreased to a constant (Schröder et al. 1998).

Particle size distribution is significantly influenced by:

- *Pore size distribution.* Uniform particle size distribution is obtained with membranes with uniform pore size distribution.
- *Distance between pores and porosity.* The controlled pore distance and the lower membrane porosity avoid droplet coalescence at the membrane pore level (Kobayashi et al. 2002).
- *Wall shear stress.* The faster is the detachment of the droplets at the membrane pore level, the lower is the droplet coalescence at the membrane surface.

Productivity is significantly influenced by:

- *Pore size, porosity, transmembrane pressure, and viscosity of dispersed phase.* As demonstrated by the Poiseuille equation, the dispersed phase flux is enhanced through the use of membranes with larger pore sizes and higher pore density, and it is proportional to the transmembrane pressure and inversely proportional to the dispersed phase viscosity.
- *Surface wetting property.* The membrane pore wall with good wettability to the disperse phase allows a quick permeation of the phase in the pores and hence results in significant higher productivity (Piacentini et al. 2014).

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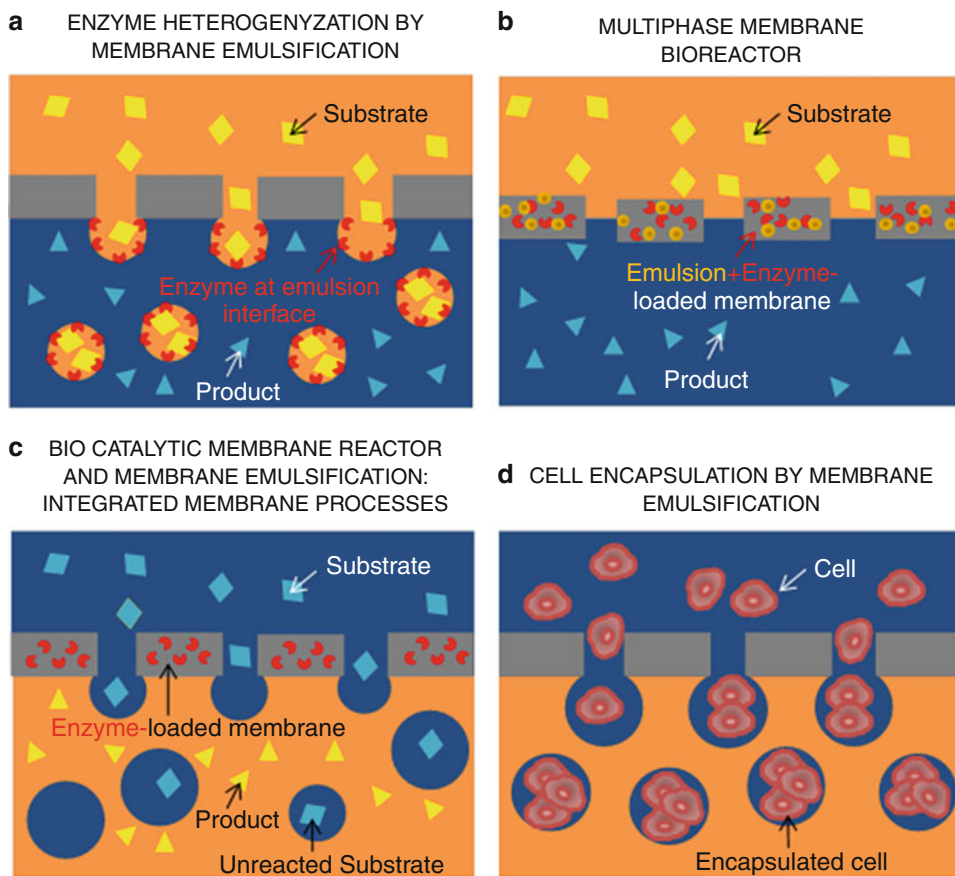
Membrane Emulsification and Biotechnological Applications

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Membrane emulsification is emerging as a unique tool for biotechnology applications. The advantages of membrane emulsification in biotechnology are related to the low shear forces on the functional and molecular properties of the biological compounds used and to the ability to tune the properties of emulsion droplets in terms of size and size distribution. Some examples include the use of membrane emulsification to assist enzymatic reaction. A simple emulsion with a heterogenized enzyme was produced using the lipase from *Candida rugosa* as model enzyme (Giorno et al. 2008) to catalyze the enantioselective hydrolysis of racemic naproxen methyl ester and produce (S)-naproxen (Fig. 1a). Lipase was distributed at the O/W interface, and the substrate of the reaction was dissolved in the dispersed phase. Emulsion droplet with controlled and uniform size provided a constant reaction interface. The enzyme optimal distribution at the interface of stable, uniform, and small droplets, produced in mild conditions able to prevent enzyme inactivation, allowed to obtain highly efficient enzymatic reaction. Microspheres with controlled size and size distribution were also prepared using membrane emulsification with different materials such as chitosan (Akamatsu et al. 2010) and polymethyl methacrylate (Omi et al. 1997), and they were used for enzyme immobilization.

O/w emulsions prepared by membrane emulsification were used in a multiphase reactor



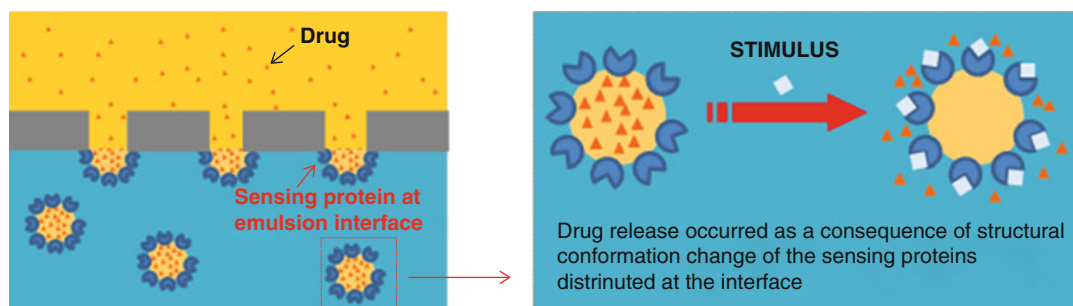
Membrane Emulsification and Biotechnological Applications, Fig. 1 Membrane emulsification application in biotechnology

(Giorno et al. 2007). The emulsion has been first loaded within the membrane together with the enzyme, lipase from *Candida rugosa*, and then the emulsion + enzyme-loaded membrane has been placed between two separate phases, an organic phase containing the substrate and an aqueous phase where the product is extracted (Fig. 1b). The emulsion allowed to optimize the enantioselective activity of the immobilized enzyme and improved the mass transfer of the hydrophobic reagent through the membrane reaction system.

The concepts of membrane emulsification and biocatalytic membrane reactor have been integrated in a single operation unit to obtain bioconversion and simultaneous separation of reaction products (having different solubility and stability in water) (Fig. 1c). The microporous membrane

structure contained the immobilized enzyme, β -glucosidase, and the permeating water reaction phase was collected as droplets into the organic phase circulated along the lumen membrane surface. The oleuropein hydrolysis into glucose and isomer of oleuropein aglycon occurred within the membrane while the aglycon was simultaneously extracted in the organic phase (Mazzei et al. 2010).

The incorporation of highly specific, high-affinity binding proteins at emulsion interface was used to produce particles able to respond to specific physiological conditions (Fig. 2). A multiple emulsion containing a bio-receptor (Con A) that specifically recognizes and interacts with an artificial ligand (glucose) was manufactured by the membrane process and used as a model system (Piacentini et al. 2011). The inner W/O emulsion



Membrane Emulsification and Biotechnological Applications, Fig. 2 Sensing emulsion droplet production by membrane emulsification

and the multiple W/O/W emulsion were both prepared using membrane emulsification method in order to control emulsion droplet size and size distribution and to preserve the functional properties of the biological components used. The drug release was promoted by the change of the interfacial structure as consequence of the Con A-glucose interaction and occurred only when the effective stimulus concentration was used.

The size-controlled production methods by membrane operation open a new opportunity also in the cell-encapsulation technology (Fig. 1d). Some examples are related to the encapsulation of probiotic bacteria. *Lactobacillus casei* was encapsulated in Ca-alginate microcapsules (Song et al. 2003). Stability tests under simulate gastric conditions demonstrated that microencapsulation technology can protect viable cells from adverse gastrointestinal conditions. Bacterial cell coming from sludge samples from a batch reactor was encapsulated in uniformly sized agarose microcapsules by membrane process, and cell viability was preserved during the preparative process (Zhou et al. 2008).

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Membrane Emulsification and Chemical Applications

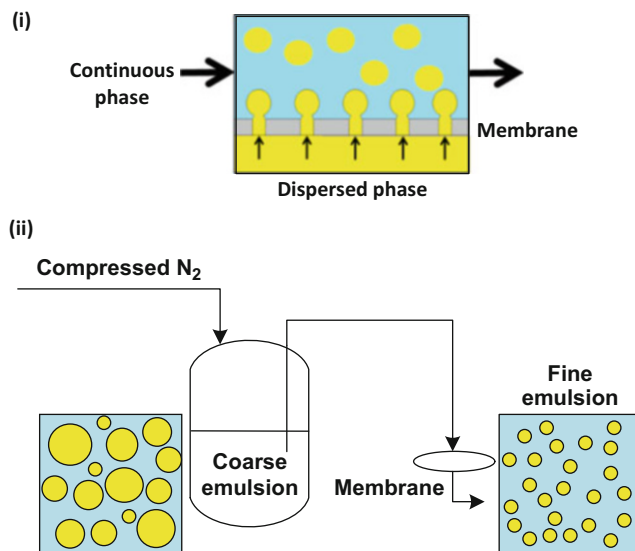
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Membrane emulsification (ME) is a technique that can be employed to produce monodisperse

Membrane Emulsification and Chemical Applications,

Fig. 1 Schematic diagram of direct ME (i) and premix ME (ii)



emulsions with controlled droplet size, low energy consumption, and low shear stress. This technique was first developed in Japan in the 1990s using the Shirasu porous glass (SPG) membranes. These membranes were capable of producing droplets ranging from 0.3 to 40 μm in diameter (Nakashima et al. 1991). SPG membranes have been widely used for the production of emulsions and for conducting chemical reactions in emulsions. Both filtration membranes and hollow fiber modules are also used today for membrane emulsification (Nakashima et al. 1991; Vladisavljevic et al. 2002).

The droplet size and droplet size distribution influence the properties of an emulsion. In some applications, such as drug delivery systems, good control over droplet size and a narrow size distribution are required to ensure efficacious activity. Several factors can affect droplet size and the droplet size distribution in ME: composition of the emulsion, membrane characteristics, equipment, and operating parameters. There are two approaches to producing emulsions with membranes (see Fig. 1): (i) *direct ME*, in which the dispersed phase is pressed through the membrane into the continuous phase, and (ii) *premix ME*, where a coarse emulsion is forced through the membrane to reduce the size of the resulting droplets.

ME has been primarily used for emulsifying edible oils in the formulation of food products (e.g., the use of milk and egg yolk proteins as emulsifiers for preparing conventional O/W and W/O emulsions). ME is also widely used to prepare emulsions for the delivery of certain pharmaceuticals. Moreover, this technique has found many applications in chemical reactions involving emulsions. A typical example is emulsion polymerization, in which SPG membranes are used to produce monodisperse microspheres (Omi 1996). A monodisperse emulsion is obtained by forcing a dispersed phase containing a monomer into a continuous phase. If a porous structure is required, the dispersed phase may also contain an initiator and a cross-linking agent. The continuous phase retains the individuality of the dispersed phase droplets that will subsequently be converted to polymeric beads. Polymerization generally starts with a change in the operating conditions that facilitate reaction throughout the entire droplet or restrict it to the surface of the droplet. Different bead structures can be generated by various changes in process conditions. Drug delivery carriers and chromatography beads have been produced by this method (Zhou et al. 2007). Furthermore, similar reactions can also occur in a double emulsion (Ma et al. 2004).

Several polymerization reactions have been performed using SPG and ceramic membranes,

but metallic membranes have been also used in either batch, cross-flow, or rotating configurations. In addition organic polymers and silica particles can be generated for subsequent functionalization (Dragosavac et al. 2012).

SPG membranes have been also applied to printer toner preparation (Kiatkamjornwong et al. 2000), while hollow particles have been used to obtain plastic pigments for paint applications. These particles provide opacity and increase brightness (Vladislavjevic and Williams 2005).

Principles involved in generating ME have been also applied to extraction coupled with enzymatic reactions. These reactions can be performed using the enzyme to stabilize the emulsion droplets (Giorno et al. 2008) or using an immobilized form of the enzyme within the pores of the membrane. In the latter case, the reaction takes place within the membrane, while the product is collected as droplets on the continuous phase side (Giorno et al. 2007; Mazzei et al. 2010).

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Membrane Emulsification and Food Applications

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Emulsion production for encapsulation and delivery of functional compounds such as vitamins or probiotics or bioactive lipids is one of the emerging fields of membrane emulsification applied to food industry. Benefits of membrane emulsification for food applications include the low shear properties and the uniform size distribution that give high encapsulation efficiency and better control of the release properties. Vitamin B₁₂ was encapsulated in multiple solid-in-oil-in-water emulsion by premix membrane (Kukizaki 2009) and in solid lipid microcapsules by two-step membrane emulsification technique (Kukizaki and Goto 2007). Astaxanthin-loaded o/w emulsions were prepared by repeated premix membrane emulsification (Ribeiro et al. 2005). *Lactobacillus casei* cells have been encapsulated in uniform emulsions and microcapsules using the membrane emulsification technique (Song et al. 2003). The aim is to increase the activity and viability of the

microorganism to the stressful conditions of the stomach and the upper intestine by encapsulation. Fish oil microcapsules were produced from oil-in-water emulsions by premix membrane emulsification (Ramakrishnan et al. 2013). The combination of a low-energy emulsification technique (premix membrane emulsification) with spray drying allowed the production of fish oil microcapsules with an oil encapsulation efficiency of more than 50 %. Fish oil-in-water emulsions containing multilayered membranes produced by premix membrane emulsification demonstrated low in vitro digestibility (Gudipati et al. 2010). Results indicated that these emulsion systems could be used to modify the release of bioactive lipids in the gastrointestinal tract.

Milk components are often used in the preparation of food emulsions. The molecular or ultrastructural status of the milk components at the fat surface plays an important role in determining the functional properties of the food products. The advantage of membrane emulsification was pointed out to be the low shear forces on the physicochemical and molecular properties of the proteins. Oil-in-water emulsions with vegetal oil as dispersed phase and a milk proteins solution as continuous phase have been prepared using SPG (Scherze et al. 1999) and ceramic membranes (Joscelyne and Trägårdh 1999). Na-caseinate and b-lactoglobulin were used also in combination with the nonionic surfactant, Tween 20, in oil-in-water emulsions preparation by membrane emulsification (Christov et al. 2002).

Membrane emulsification has been tested also in the preparation of specific emulsion-based food product such as foamed food products like chocolate mousse, ice cream, or fresh cheese and low-fat product such as double emulsions and spread. Foamed food product where air is present as a component of several food products present (dispersed phase of bubbles or pores) was produced by membrane foaming. The method is based on pressing the dispersed phase as a form of gas through the membrane pores into the continuous phase while the continuous phase, containing whey proteins as surface-active substances, flowed along the membrane surface (Bals and Kulozik 2003a, b). Rotating membrane

emulsification was also used in the preparation of gas dispersion to improve the foam microstructure in terms of size and size distributions (Müller-Fischer et al. 2007). The Morinaga Milk Industry (Japan) developed and commercialized a low-fat spread using membrane technology (Okonogi et al. 1992). The volume fraction of dispersion water-phase reaches up to 75 % and the product is reported to be very stable, with suitable texture, and tasty. The potential for the easy scale-up is another attractive quality of membrane emulsification technology. Microencapsulation of vegetable oil droplets using cold water fish gelatine/gum arabic complex coacervation has been obtained at batch and large scale production using the stirred and the pulsed flow membrane emulsification (Piacentini et al. 2013).

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Membrane Emulsification and Pharmaceutical Applications

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Conventional oral drug administration methods, such as solutions, suspensions, tablets, and capsules, often do not provide protection from the acidic environment present in the stomach (Hillery et al. 2002) and do not provide a constant therapeutic blood concentration of the drug over time (Hoffman 2008). A re-administration of the drug is required, and the possibility of drug reaching the toxic levels is often high. Formulation of particles for the purpose of drug release systems has received increased interest over recent years (Freiberg and Zhu 2004). Encapsulating the drug (pharmaceutical) into particles of suitable size makes it possible to tailor the release, obtaining a site-specific release, prolonged action, and/or sustained release (Saltzman 2001).

In the physical sciences, a particle represents a small localized object to which can be ascribed several physical properties such as volume or mass. Particles may be solid, but they also may be liquid droplets dispersed in another immiscible

liquid or air. An emulsion is a dispersion of one liquid in another where the liquids are not miscible or are slightly soluble, and they play a valuable role in the production of the particle. Emulsion droplets are already particles, but, even more, the droplets after production may be converted into solid particles, suitable for the encapsulation within the core material (Hillery et al. 2002), by applying additional physical (fluidized bed coating, spray or freeze-drying, evaporation/solvent diffusion) or chemical (coacervation and interfacial polymerization) treatments.

The choice of the emulsification process is a key issue in the encapsulation as it influences directly the final size, and size distribution, of the solid particles. Some important challenges are required for the advancement of microencapsulation technologies in engineering microcapsules with improved functional and structured properties (Imbrogno et al. 2015):

- (i) Achieving precise control of particle size and size distribution in the emulsification step while maintaining the incorporation of biomolecules without affecting their activity, the distribution in the body, and the interaction with living cells as well as the drug release kinetics of the solid particles are greatly influenced by their size and uniformity (Huang et al. 2008).
- (ii) Maintaining the performance of a good emulsification step when the process is transferred from the laboratory scale to a larger throughput scale (Benita 2006; Dragosavac 2011).

Conventional emulsification processes such as high-shear rotor–stator mixers, high-pressure valve homogenizers, and ultrasonic and static mixers apply more energy than needed to disrupt the droplet, and the droplet breakup is mainly due to the turbulent eddies (Karbstein and Schubert 1995). In such devices, a premix is necessary, which is produced by gentle mixing, followed by homogenization which will lead to further reduction of the droplet size. In general, homogenization is an intense process: it introduces a large amount of energy into the premix emulsions to break the droplets into smaller ones (Dragosavac

2011). Conventional emulsification systems (Karbstein and Schubert 1995) are very convenient for production of droplets below 10 μm . For production of larger droplets (greater than 10 μm), low shear needs to be applied, but conventional homogenization in that case produces droplets with a wide size distribution. Such product is often unstable and has unsatisfactory properties.

By contrast, membrane emulsification (Nakashima et al. 1991) is a mild dispersion process to produce a monosized emulsion of one liquid phase in a second immiscible liquid phase using low energy per unit volume (Giorno et al. 2009; Vladisavljević and Williams 2005). The dispersed phase is pressed through the membrane into the continuous phase, and it is widely accepted that shear on the membrane surface needs to be applied in order to produce uniform droplets, and the growth and detachment of the droplets is a complex phenomenon dependent on the process conditions including the formulation of the dispersed and the continuous phases. Compared to conventional emulsification systems, membrane emulsification devices operate under constant temperature due to mild shear conditions, keeping heat and shear-sensitive ingredients intact and providing high encapsulation yields of multiple emulsions (Dragosavac 2011).

Numerous simple emulsions have been prepared using membrane emulsification w/o (Liu et al. 2008; Vladisavljević et al. 2002) and o/w (Vladisavljević and Williams 2010). The mild conditions of membrane emulsification are especially useful when the microencapsulation process involves the preparation of a multiple emulsions. Multiple emulsions are complex systems, termed “emulsions of emulsions” where droplets contain even smaller dispersed droplets within themselves (Garti 1997). Multiple emulsions have significant potential in many applications since they can serve as an entrapping reservoir for active ingredients that can be released from the inner phase to the outer phase by a controlled and a sustained mechanism (Garti 1997) suitable for pharmaceuticals. Most common multiple emulsions are

W/O/W emulsions (small water droplets dispersed within the larger oil droplet). This kind of emulsion is highly thermodynamically unstable, and emulsion breakdown can occur easily in the high shear stress conditions; therefore, the production by membrane emulsification is highly beneficial. W/O/W emulsions are produced by forcing the primary (W/O) emulsion through hydrophobic membrane into continuous phase. Lower shear (compared to conventional methods) is applied above the membrane surface to detach the droplets which are intact and have high encapsulation efficiency (Dragosavac 2011). Selecting the operating conditions (pore size and shear applied), it is possible to tune the final droplet size, and the process can be scaled up, keeping the performance demonstrated at the laboratory scale (Dragosavac 2011; Charcosset 2009). So far, membrane emulsification has been investigated for microencapsulation of water-soluble and lipophilic drugs within W/O/W emulsions such as ethanol–oil–water E/O/W and water–oil–water W/O/W (Vladisavljević and Williams 2005; Nakajima 2003) or within microspheres and capsules produced in most cases by coacervation, interfacial polymerization, and solvent evaporation (Huang et al. 2008; Charcosset 2012; Piacentini et al. 2013; Vladisavljević 2015).

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Membrane Emulsification Applications

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Membrane emulsification (ME) is used in the preparation of simple emulsions, multiple emulsions, foams, liposomes, coherent solids, and structured solid (Vladisavljević and Williams 2005; Table 1).

The range of application areas of ME includes (Giorno et al. 2009; Piacentini et al. 2010):

- Food

Emulsions are used in the preparation of dressings, artificial milks, cream liqueurs, margarines, and low-fat spreads. Sensitive food materials and flavors can be encapsulated to enhance the sensory perception. One example at industrial scale is the development and commercialization of a very low-fat spread using ME technology by Morinaga Milk Industry (Japan).

- Pharmaceutical

The drug-delivery system is one of the most attractive fields of ME. Emulsions and structured solidified particles have been prepared to transport and deliver anticancer drug, proteins, vitamins, and probiotics. $W_1/O/W_2$ emulsions have been prepared to transport and deliver anticancer drug for liver cancer treatment followed by clinical study.

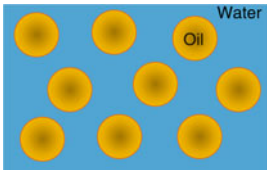
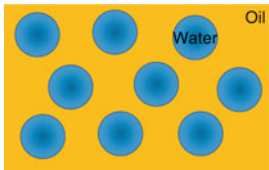
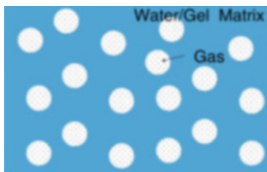
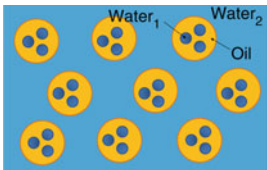
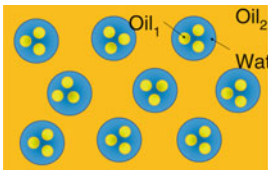
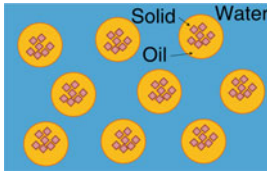
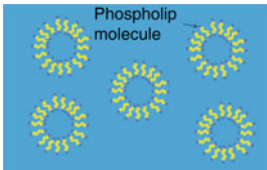
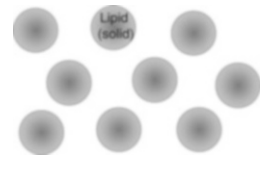
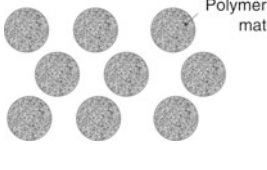
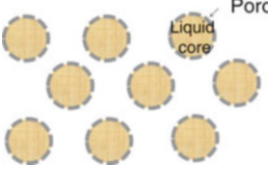
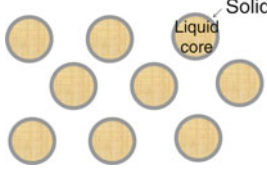
- Cosmetic

Emulsion for the treatment, protection, care, and/or cleaning of the skin, mucous membranes and/or hair, and/or as makeup for the skin and/or mucous membranes have been prepared by ME.

- Other application

ME has been used in the preparation of emulsion fuel and photosensitive material.

Membrane Emulsification Applications, Table 1 Emulsions and particulate products produced by using membrane emulsification

Membrane emulsification applications		
Simple emulsions		Foam
Oil-in-water emulsion (O/W) 	Water-in-oil emulsion (O/W) 	
Multiple emulsions		Solid-in-oil-in-water dispersion (S/O/W)
Water-in-oil-in-water emulsion ($W_1/O/W_2$) 	Oil-in-water-in-oil emulsion ($O_1/W/O_2$) 	
Liposomes 	Coherent solids	
	Metal solder particle 	Solid lipid microspheres 
Structured solid		
Polimeric or gel microbeads 	Porous core-shell microcapsules 	Nonporous core-shell microcapsules 

The technology was demonstrated to be suitable in the construction of multiphase reaction systems using phase transfer (bio)catalysts and in combination with liquid–liquid extraction and enzymatic reaction to achieve simultaneous drop generation, chemical conversion, and interfacial mass transfer.

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Membrane Emulsification in Phase Separation for Microcapsule Preparation

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Synonyms

Coacervation; Core shell particles

Microencapsulation is described as a process of enclosing micron-sized particles of solids or droplets of liquids or gasses in an inert shell, which isolates and protects them from the external environment. Microcapsules (particles size in the range between 3 and 800 μm) consist of an inner core (in which the active molecule is entrapped) and a shell that covers and protects the core. Different types of molecules like active pharmaceutical compounds, proteins, peptides, volatile oils, food materials, pigments, dyes, monomers, catalysts, pesticides, etc. can be encapsulated with different types of shell materials that in most cases are natural or synthetic polymers.

The majority of the methods achieved for the preparation of microcapsules are based on the preparation of an emulsified system, in the first step, and the formation of the shell, in a second step. The shell formation can be obtained (i) by precipitation or gelation of a polymer around the core (coacervation or phase separation), (ii) by polymerization of monomers at the interface of two immiscible phases (interfacial

polymerization), and (iii) by evaporation of the solvent with the concomitant solidification of the polymeric shell around the core (solvent evaporation) (Jyothi et al. 2010).

The term phase separation describes a process in which a polymer solution separates in two immiscible phases (a polymer-rich phase and a polymer-poor phase) after a perturbation of the equilibrium of the system. The preparation of microcapsules with this method consists in three basic steps: (i) dispersion of the core material in a coating material of polymer solution (emulsification step), (ii) deposition of the coating material around dispersed solid particles or liquid droplets by inducing a separation of two immiscible phases, and (iii) hardening of the coating by cross-linking or thermal treatment.

Membrane emulsification can be used in the emulsification step to finely control the dispersion of the core material into the solution of coating material. This method basically consists in the permeation of the dispersed phase through a porous membrane to form droplets at the opening pore and the subsequent detachment from the membrane surface into the continuous phase. A distinguishing feature of membrane emulsification is the possibility to control the resulting droplet size by the optimization of membrane parameters (porosity, mean pore size, pore geometry, pore distance, wettability) and process parameters (wall shear stress, transmembrane pressure, membrane module configuration, temperature) and not by the generation of turbulent droplet breakup which characterizes conventional methods (stirring, sonication, homogenization). The controlled delivery of substances encapsulated in the core of microcapsules is highly dependent on the uniformity in shape and size of microcapsules. Membrane emulsification is an advantageous technique because of its effectiveness in producing narrow droplet size distributions at low-energy consumption and mild shear conditions, making it potentially suitable for the encapsulation of shear-sensitive compounds.

The formation of the shell material around the droplet of the core material can be induced by altering chemical or physical parameters on the basis of the nature of the polymer and the kind of

the polymeric system (see Table 1). From a thermodynamic point of view, a polymeric system can be distinguished in:

- *Binary system*, consisting of one polymer dissolved in a solvent
- *Ternary system*, consisting either of a single polymer in a binary solvent mixture or of two polymeric components in a single solvent

Salting out consists in the addition of concentrated electrolyte solution (such as sodium sulfate) to the polymer solution in order to induce a desolvation of the polymer that precipitates on the droplets of the core material (see Fig. 1). This kind of process is usually used to induce

the phase separation of the system containing gelatin in the aqueous phase.

The variation of pH can be applied either for binary system to induce the phase separation of polymer solution that has a water solubility pH dependent (such as chitosan; see Fig. 1) or for ternary system to induce the electrostatic interaction between polyelectrolytes with opposite charge (polyanion and polycation). The latter method is also known as “complex coacervation,” and gelatin/acacia (Arabic gum) is the most common system used for the preparation of microcapsules with this method. The interaction between the polymers can be induced by pH adjustment from a value at which the polymers carry the same charge to a value at which both polymers carry net opposite charge (see Fig. 2a).

A demixing of binary system can also be obtained by a reduction of the temperature of the system until a critical value at which the polymer solution is thermodynamically unstable and separates spontaneously in two liquid phases. The formation of a polymer film occurs through the growth of nuclei of concentrated polymer (see Fig. 1).

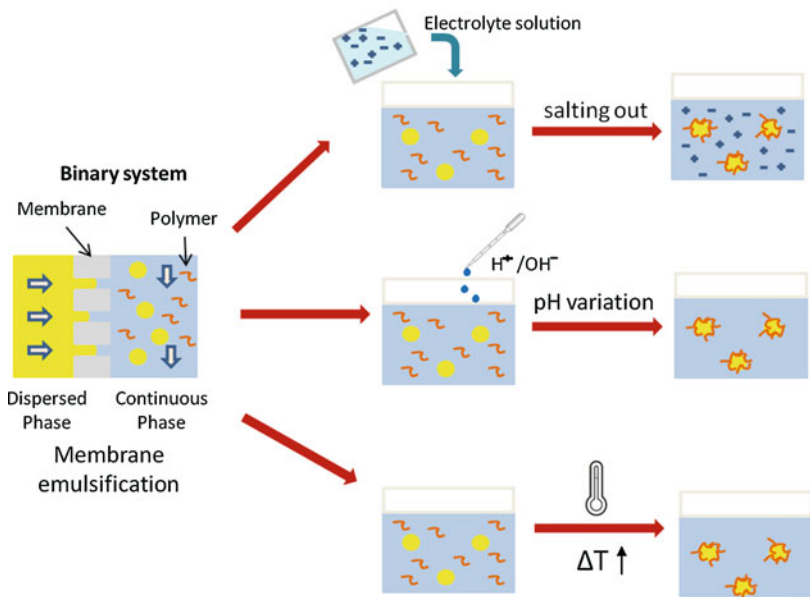
Besides temperature variation, a demixing of the polymer solution can also be achieved by the addition of a third component (nonsolvent) in

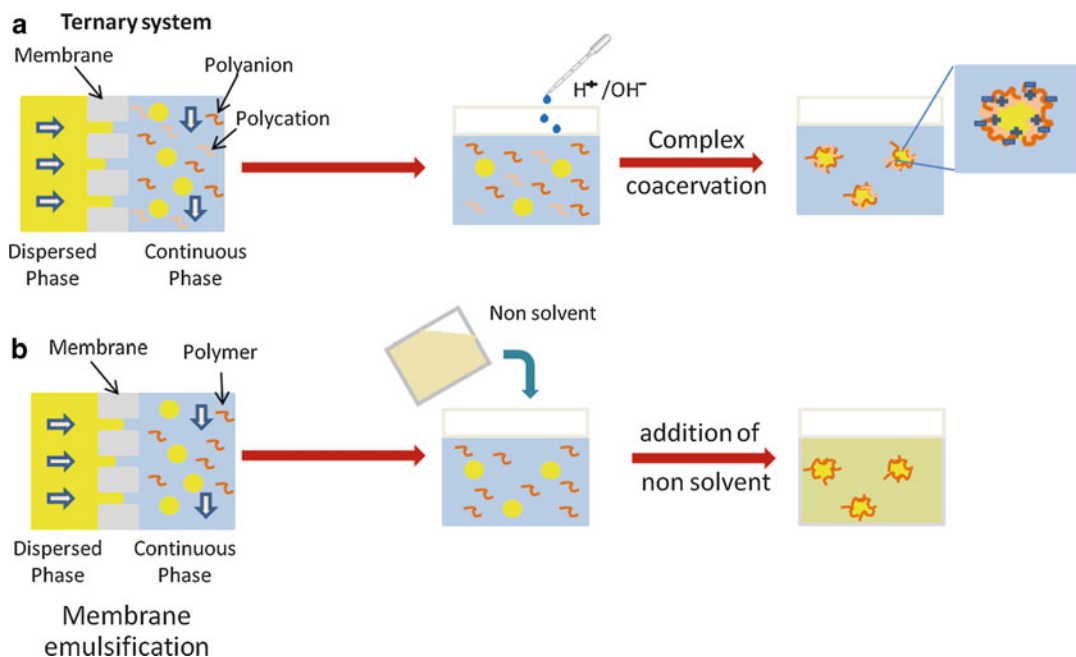
Membrane Emulsification in Phase Separation for Microcapsule Preparation, Table 1 Parameters to induce phase separation of polymer system

Polymer system	Phase separation process
Binary system	Salting out
	Variation of pH
	Variation of temperature
Ternary system	Induction of polymer-polymer interaction
	Addition of nonsolvent

Membrane Emulsification in Phase Separation for Microcapsule Preparation,

Fig. 1 Production of microcapsules by membrane emulsification and phase separation from binary system: salting-out, pH variation, temperature variation





Membrane Emulsification in Phase Separation for Microcapsule Preparation, Fig. 2 Production of microcapsules by membrane emulsification and phase

separation from ternary system: a) complex coacervation; b) addition of non-solvent

M

which the polymer is insoluble but the solvent is miscible. In this case, we have a ternary system of polymer, solvent, and nonsolvent, and the demixing in two liquid phases occurs when the nonsolvent overcomes a critical volume at which the system is thermodynamically unstable (see Fig. 2b). The formation of the polymer film around the core material is based also in this case on nucleation and growth of nuclei of polymer-concentrated droplets. This method can be used for the preparation of microcapsules with either an oil or aqueous core. In the first case, gelatin, polyvinyl alcohol, and ethyl cellulose dissolved in an aqueous phase are commonly used as coating material, and the addition of water-soluble solvent (such as ethanol, propanol, and acetone) induces the phase separation of the polymer solution. In the second case, hydrophobic polymers (such as biodegradable polyesters) are dissolved in solvent partially soluble in water (such as dichloromethane and ethylacetate) and are used as organic phase for the preparation of a

W/O/W double emulsion. The precipitation of the polymer occurred at the interface between the internal aqueous phase (core material) and the organic phase (coating material) after the addition of a nonsolvent (Arshady 1990, 1991; Gander et al. 2007; Olabis 2012).

An innovative method in which polymeric microsphere generation has been obtained by combining membrane emulsification process with phase separation induced in a single step is reported by Piacentini et al. (2013). In this case, a nonaqueous (O/O) emulsion is generated by injecting the polymeric solution through a microporous membrane into the nonaqueous continuous phase that works at the same time as phase separation inducer and allows the particle formation. In this case, droplet formation and solidification occur in a single step.

In Table 2 are reported some works in which microcapsules are prepared using membrane emulsification and phase separation.

Membrane Emulsification in Phase Separation for Microcapsule Preparation, Table 2 Examples of microcapsules produced by membrane emulsification/phase separation

Particles type	Emulsification process	Phase separation process	References
Microcapsules with an oil core and gelatin/Arabic gum shell	Stirrer ME, microchannel emulsification	Complex coacervation	(Piacentini et al. 2013) (Nakagawa et al. 2004)
Chitosan hollow microcapsules	SPG ME	Alginate/chitosan electrostatic interaction	(Akamatsu et al. 2010)
Alginate microcapsules	Microporous glass ME	Salting out	(Song et al. 2003)
Ethyl cellulose hollow microcapsules	Microfluidic emulsification	Addition of nonsolvent	(Liu et al. 2009)
Poly lactide microcapsules	Premix ME, microfluidic emulsification	Addition of nonsolvent	(Sawalha et al. 2008) (Watanabe et al. 2013)
Polyethersulfone (PES) microspheres	Stirrer ME	Addition of nonsolvent	(Piacentini et al. 2013)

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Membrane Emulsification Modeling

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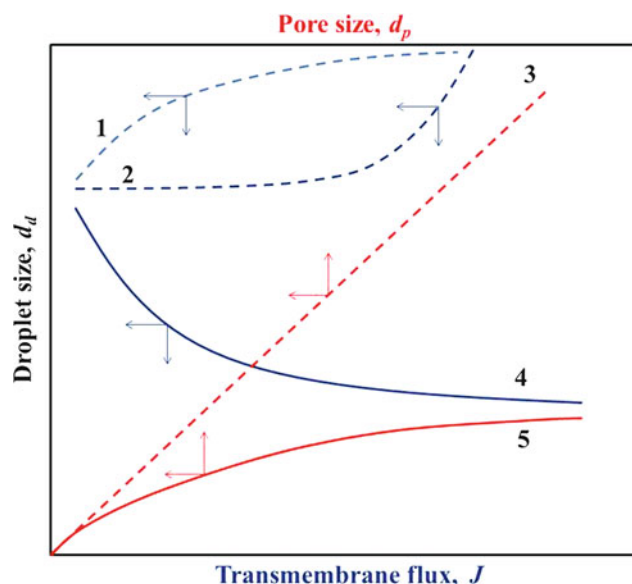
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Membrane emulsification (ME) process is governed by a significant number of variables that can be divided into membrane parameters (wettability, charge, porosity, pore size, pore morphology, and spatial arrangement of the pores),

Membrane Emulsification Modeling,

Fig. 1 Mean droplet size, d_d , in direct membrane emulsification (DME) (dashed lines) and premix membrane emulsification (PME) (solid lines) as a function of mean pore size, d_p , of the membrane and transmembrane flux, J : (1) d_d vs. J in shear-controlled DME; (2) d_d vs. J in DME, spontaneous drop detachment; (3) d_d vs. d_p in DME; (4) d_d vs. J in PME; and (5) d_d vs. d_p in PME. Reproduced with permission from Vladislavjević et al. (2015)



formulation parameters (viscosity of the dispersed and continuous phase, a nature of the surfactant used, surfactant concentration, etc.), and process parameters (shear generated on the membrane surface, transmembrane flux, etc.). The droplet size in direct membrane emulsification (DME) has been predicted analytically, using force and torque balance models (Timgren et al. 2010; De Luca et al. 2008; Williams et al. 1998), and computationally, using computational fluid dynamics (CFD) simulations (Kobayashi et al. 2004; Abrahamse et al. 2001) and the Surface Evolver software (Rayner et al. 2004).

Two mechanisms of drop detachment from the pores in DME have been identified: (a) shear-controlled detachment as a result of shear stress on the membrane surface and (b) spontaneous detachment driven by interfacial tension (Sugiura et al. 2002). In DME, a linear correlation between the mean droplet size and the mean pore size exists in dripping regime: $d_d = Kd_p$ (line 3 in Fig. 1), where K typically ranges between 2 and 6. In premix membrane emulsification (PME), the mean droplet size is a nonlinear function of the mean pore size (line 5 in Fig. 1): $d_d = K'(d_p)^n$, where $n < 1$. The d_d/d_p ratio decreases with increasing the mean pore size and the shear stress on the pore walls and ranges between 0.5 and 1.5.

In the shear-controlled DME process at $J \rightarrow 0$, the mean droplet size is determined by a balance between the shear force exerted on the liquid-liquid interface by the continuous phase and the capillary force. The mean drop size decreases with increasing shear stress on the membrane surface until it reaches a constant value at high shear stresses. The resultant drop size at $J > 0$ is greater than that at zero flux, because a droplet will continue to increase in size during the detachment period as a result of inflow of the dispersed phase via the droplet neck. The volume of the dispersed phase flowing into the droplet during the detachment phase increases with increasing the dispersed phase flow rate, and thus, the resultant drop size increases with increasing the transmembrane flux (line 1 in Fig. 1). At high transmembrane fluxes, the push-off force as a result of droplet-droplet interactions on the membrane surface should be added to the shear force in the shear balance model, causing a plateau region to occur on a d_d vs. J plot at high transmembrane fluxes (line 1 in Fig. 1) (Egidi et al. 2008). In the spontaneous droplet detachment process, the detachment period is very short, so the resultant drop size in dripping regime is virtually independent on the transmembrane flux (line 2 in Fig. 1).

In PME, the mean droplet size decreases with increasing the transmembrane flux (line 4 in Fig. 1) due to an increased shear stress within the pores at the higher flux. PME was modeled using the modified resistance-in-series model to account for droplet disruption (Vladisavljević et al. 2004) or energy density concept (Nazir et al. 2011).

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Membrane Emulsification Principles

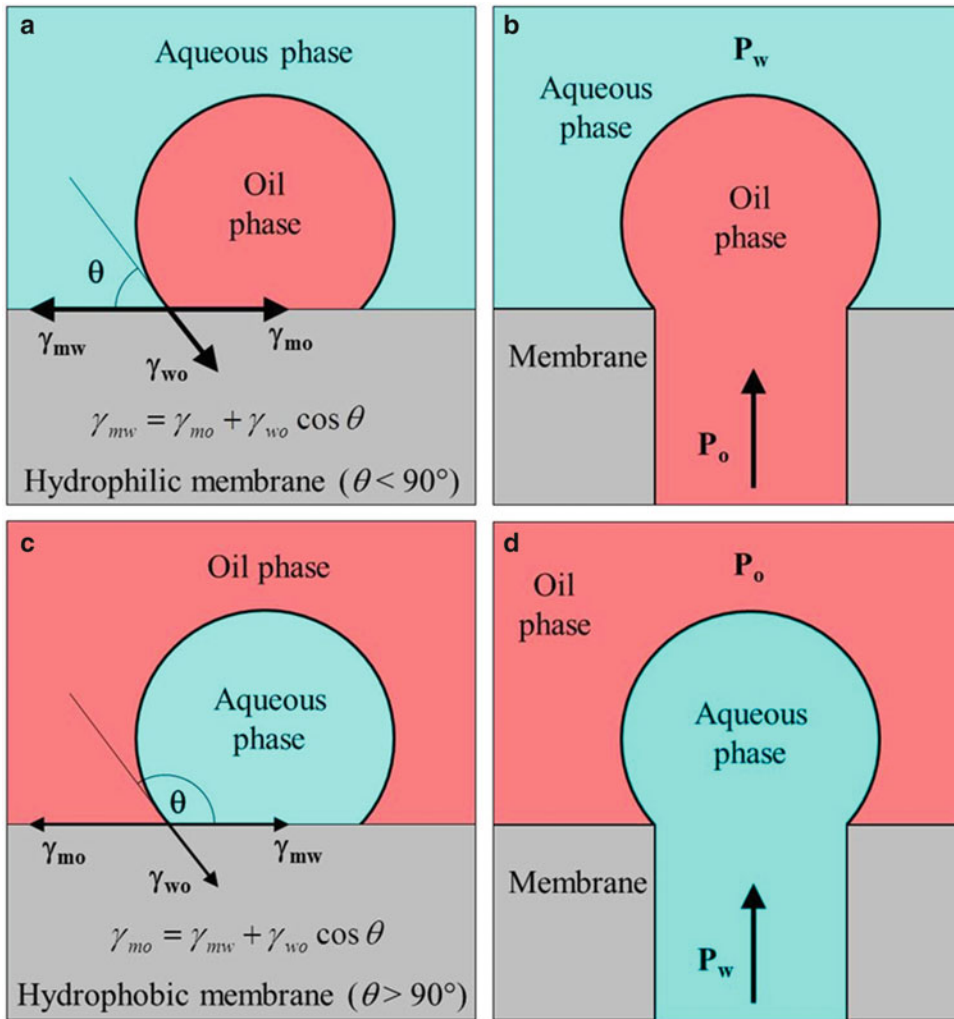
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Membrane emulsification (ME) is an emerging technology of droplet generation in which a dispersed phase or premix is forced through the pores of a microporous membrane into a continuous phase. In contrast to traditional approach of breaking and re-breaking droplets into successively smaller droplets until the desired droplet size range is achieved (Karbstein and Schubert 1995), ME creates each droplet directly at the final desired size without intermediate disruption and re-coalescence. This “made-to-measure” production approach requires less energy input and offers greater control over emulsion droplet size. ME is suitable when dealing with emulsions prone to disintegration, such as multiple emulsions (Surh et al. 2007; Dragosavac et al. 2012) and emulsions containing shear- and heat-sensitive ingredients. A shear rate on the membrane surface in direct ME is in the range of $(1\text{--}50) \times 10^3 \text{ s}^{-1}$, but droplets can be produced even in the absence of shear, while in high-pressure valve homogenizers, such as Microfluidizer[®], the shear rate can be as high as 10^7 s^{-1} . Energy input in conventional emulsification devices is spatially nonuniform leading to the production of polydispersed emulsions. In ME the shear is uniformly distributed over the membrane surface and precisely controlled by cross flow of the continuous phase, stirring rate or the rate of membrane oscillation or rotation. Cross-flow ME resembles microfluidic T junction; the main difference being that in cross-flow ME, the droplets are simultaneously formed from many different pores, and



Membrane Emulsification Principles, Fig. 1 (a) Oil droplet immersed in an aqueous phase and resting on a nonporous hydrophilic membrane surface; (b) Production of oil droplet by injecting oil phase through a hydrophilic pore into an aqueous phase; (c) Water droplet immersed in

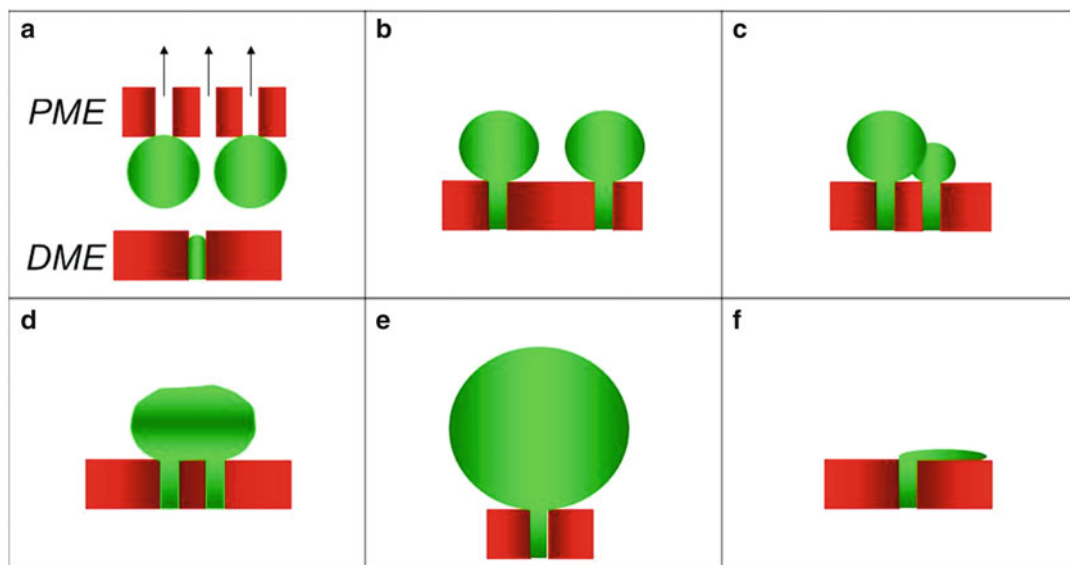
an oil phase and resting on a nonporous hydrophobic membrane surface; (d) Production of water droplet by injecting aqueous phase through a hydrophobic pore into an oil phase

the cross-sectional area A_{ch} of the cross-flow channel is large compared to the cross-sectional area A_p of the pore ($A_{ch}/A_p > 1000$). Thus, the forming droplets are not confined by the walls of the cross-flow channel, and the drop generation mechanism differs to that in T junction (Vladislavjević et al. 2012).

The minimum transmembrane pressure for driving a pure oil phase through the pores with a diameter of d_p is the capillary pressure, P_{cap} , given by the Young-Laplace equation:

$$P_{cap} = \frac{4\gamma_{wo} \cos \theta}{d_p}$$

where γ_{wo} is the equilibrium interfacial tension between the water and oil phase and θ is the contact angle, i.e., the angle formed by a water phase at the three-phase boundary where the water phase, oil phase, and membrane intersect (Fig. 1a and c). A hydrophilic membrane ($\theta < 90^\circ$) is used in the production of O/W emulsion (Fig. 1b), and thus $P_{cap} > 0$ and $P_o > P_w$.



Membrane Emulsification Principles, Fig. 2 Droplet formation behavior in membrane emulsification: (a) critical pressure not exceeded (DME direct ME, PME premix ME); (b) optimal drop generation behavior (droplets do not interact with membrane surface or neighboring droplets);

(c) steric hindrance caused by small interpore distance compared to droplet diameter; (d) droplet coalescence on the membrane surface; (e) continuous outflow of the dispersed phase; (f) spreading of the dispersed phase on the membrane surface

A hydrophobic membrane ($\theta > 90^\circ$) is used in the production of W/O emulsion (Fig. 1d), and thus $P_{\text{cap}} < 0$ and $P_o < P_w$, i.e., the water phase pressure should be higher than the oil phase pressure by P_{cap} to drive the water phase through the membrane.

The capillary pressure in premix ME (PME) is given by (Park et al. 2001):

$$P_{\text{cap}} = \frac{\gamma_{wo} \left[2 + 2a^6 / \sqrt{2a^6 - 1} \times \arccos(1/a^3) - 4a^2 \right]}{a + \sqrt{a^2 - 1}}$$

where $a = d_1/d_p$ and d_1 is the mean droplet size in premix. The capillary pressure in PME is lower than that in DME, but for $d_1/d_p \gg 1$, the two capillary pressures are the same.

Different droplet formation behaviors in ME are shown in Fig. 2. If the transmembrane pressure is lower than P_{cap} , the dispersed phase will not pass through the pores in DME, and the membrane will reject the droplets in PME, which will lead to the separation of the premix into droplet-free continuous phase and concentrated emulsion (Koltuniewicz et al. 1995).

Uniform droplets are formed under optimum range of process parameters providing that the product formulation and membrane properties are appropriate (Fig. 2b). The problems associated with ME are steric hindrance between the droplets on the membrane surface as a result of insufficient distance between the pores (Fig. 2c), droplet coalescence due to poor stabilization of newly formed interface by surfactant molecules (Fig. 2d), continuous outflow of the dispersed phase (Fig. 2e), and droplet spreading on the membrane surface caused by the wetting the membrane surface by the dispersed phase (Fig. 2f).

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Membrane Engineering

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The way to satisfy the increasing demand for raw materials, energy, and products under the constraints imposed by the concept of sustainable development is a complex problem; possible solutions can be found through rational integration and implementation of new industrial, economic, environmental, and social strategies. A possible route to a more sustainable industrial growth is offered by the process intensification strategy, which is a design approach aimed at leading to concrete benefits in manufacturing and processing, substantially shrinking equipment size, boosting plant efficiency, saving energy, reducing capital costs, minimizing environmental impact, increasing safety, using remote control and automation, etc. (Drioli et al. 2011).

In this context, an interesting and important case is the continuous growth of modern membrane engineering, whose basic aspects satisfy the requirements of process intensification. In fact, it is well recognized that membrane processes have the potential to replace conventional energy-intensive separation techniques, such as distillation and evaporation, to accomplish the selective and efficient transport of specific components, to improve the performance of reactive processes, and, in the ultimate instance, to provide reliable options for sustainable industrial growth (Drioli and Giorno 2010).

Membrane operations, such as molecular separations, catalytic membrane reactors, membrane contactors, etc., with their intrinsic characteristics of efficiency and operational simplicity, compatibility between different membrane operations in integrated systems, low energy requirements, good stability under operative conditions, environmental compatibility, easy control and scale-up, and large flexibility, offer an interesting answer for advanced rationalization of a large variety of industrial processes.

In several different fields, these potentialities have already been realized. The growth in membrane installations for water treatment, for example, has been exponential over the past decade; this has resulted in decreased cost of desalination facilities, with the consequences that the cost of reclaimed water from membrane plants also has been reduced. Today, membrane technology is recognized as the most convenient approach in desalination, producing daily more water than thermal systems (Koltuniewicz and Drioli 2008; Macedonio et al. 2012; Strathmann et al. 2006).

Other areas, such as biochemical engineering, regenerative medicine, packaging, petrochemical industry, etc., have seen continuous innovations that, in the future, will lead to significant increased utilization of membrane operations in these sectors.

The term membrane engineering is becoming largely used and common for representing the engineering discipline covering all the membrane operations from pressure-driven membrane operations such as RO, NF, MF, UF, and gas separations to energy productions and membrane reactors, membrane distillation, and additional

types of membrane contactors. These membrane processes have all the possibility to replace conventional chemical unit operations.

The increased attention toward membrane engineering is also noticed by the establishment of a section on membrane engineering in the European Federation of Chemical Engineering (EFCE) founded in 2007, with the objective to promote strategic collaboration between experts in membrane engineering and related areas for addressing solutions and strategies interconnected to the membrane field.

Furthermore, a European Union-funded doctorate in the framework of the Erasmus Mundus program has been created to develop high-level education in the field of membrane engineering (Erasmus Mundus Doctorate in Membrane Engineering – EUDIME) with the aim to implement excellence, innovation, mobility, and multidisciplines related to membrane engineering.

Basic unit operations in process engineering such as distillation, crystallization, emulsification, condensers, etc., have here redesigned as membrane distillation (MD), membrane crystallization (MCR), membrane emulsifier (ME), membrane condenser (MC), etc. They are attracting growing attention. The development of integrated membrane operations in desalination, in fuel cells, in agro-food processes, etc., is becoming interesting industrial realities.

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Membrane Extractor as a Configuration of Membrane Reactor

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Numerous practice-relevant reactions like dehydrogenations, esterifications, steam reforming Knoevenagel condensation, or thermal water splitting take place in industry under thermodynamic control. This means, there exists an equilibrium between products and educts due to $A + B \leftrightarrow C + D$ defined by $r_{RG} = -RT \ln K$ with r_{RG} as the Gibbs Energy (Free Enthalpy) of the reaction and K as the equilibrium constant. The “membrane extractor” concept is based on the selective in situ extraction of one or of both products C and/or D under equilibrium controlled reaction condition from the feed A, B . The main advantage of this concept is an enhancement of the conversion and increase of the yield (Dittmeyer and Caro 2008; Caro 2010). By the removal of C and/or D , sometimes also the selectivity is influenced.

The reaction must be sufficiently fast compared to the mass transport through the membrane, a feature called “kinetic compatibility.” Higher conversion – and thus yield – due to the beneficial effect of product removal may lead to savings on energy and raw materials, especially if the component removed through the membrane is pure enough for further applications. Historically, the selective hydrogen removal in alkane dehydrogenations to the corresponding olefins thus overriding the equilibrium constraint was the most studied membrane extractor case. The most prominent “membrane extractor reactors” studied at present are reformers for the production of fuel-cell-grade hydrogen from hydrocarbons or alcohols using Pd-based membranes. The removal of water through hydrophilic membranes in esterifications is another prominent example of “membrane extractor reactors.”

Besides conversion enhancement, also selectivity increase can take place in membrane extractors. For example, in Fischer–Tropsch synthesis, the removal of the by-product water has several advantages on the reactor performance like reduced catalyst deactivation or lowered kinetic inhibition.

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Membrane Fermentors

► Membrane Bioreactors

Membrane Filtration in Biorefinery

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Membrane filtration in biorefinery is the application of membrane separation technology in various stages of biorefining processes for process intensification, product recovery and purification, and bioenergy production. Membrane filtration is a separation technique that separates particles from a liquid by using a porous material. The liquid can pass through the pores of the membrane, while particles are retained by the membrane. A number of specific membrane processes are of particular value for biorefining and bioenergy production: microfiltration (MF) (pore size, 0.1–10 μm), ultrafiltration (UF) (pore size, 2–100 nm), nanofiltration (NF) (pore size,

1–2 nm), pervaporation (PV), membrane distillation (MD), and diafiltration (DF). The MF, UF, and NF processes use porous membranes and are driven by hydrostatic pressure; PV uses nonporous membranes and is driven by a chemical potential gradient, while MD uses porous hydrophobic membranes and is driven by a thermal gradient. DF uses porous membranes to remove salts or solvents from solutions based on molecular sizes. Among the various separation technologies used in biorefinery, membrane technologies provide excellent fractionation and separation capabilities, low chemical consumption, and reduced energy requirements.

In integrated forest biorefinery, MF and UF have been extensively studied for lignin and hemicellulose recovery and purification from kraft mill black liquor, spent sulfite liquor, and thermomechanical pulping's spent liquor (He et al. 2012). Furthermore, membrane filters are used in commercial production of lignins from kraft pulp black liquors (Kouisni and Paleologou 2010). In bioenergy production, membrane separations have been widely used in bioethanol production, including removal of fermentation inhibitors, enzyme recovery from the hydrolysis processes, membrane bioreactor for bioethanol production, and dehydration of bioethanol (Abels et al. 2013). In biogas production, anaerobic membrane bioreactors (AnMBR) have been successfully used for bioenergy recovery and water reuse from food processing wastewater (Christian et al. 2010) and alcohol stillage wastewater treatment (Grant et al. 2008). In bio-oil and biodiesel production, MF was examined for char particles from bio-oil, the liquid product from the pyrolysis of renewable biomass (Hoekstra et al. 2009); membrane reactor has been used for biodiesel production from waste vegetable oils and animal fats (He et al. 2012). Furthermore, membrane filtration has been used for separation and purification of biodiesel product by removing glycerol (Gomes et al. 2010). In algae production, membrane filtration has been studied for algal harvesting and dewatering to save energy (Bhave et al. 2012), purification of pigments from macroalgae (Denis et al. 2009), and recovery of triacylglycerols from wet microalgae for biodiesel production (Giorno

et al. 2013). It is anticipated that membrane filtration will play a significant role in biorefinery operations in the near future.

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Membrane Fouling During Wine Processing

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Microfiltration was the first to be applied for wine clarification with membrane pore sizes from 0.2 to 1.2 μm . Nowadays, membranes are largely used in enology for must, lees, and wine in various applications. Membrane fouling results from complex interactions between macromolecular adsorption or deposition, internal fouling, and cake formation by the retained compounds. The respective impact of these different fouling mechanisms strongly depends on the composition of the fluid to be filtered, on the membrane characteristics, on the hydrodynamic conditions, as well as on the physical-chemical interactions between the fluid components and the membrane surface and between these components themselves. Membrane fouling may be induced by the adsorption of wine macromolecules and colloids to the membrane surface or within the membrane pores. Colloids in wine are pectic substances, yeast polysaccharides, proteins, and molecular aggregates resulting from the association of small solutes such as polyphenol aggregates. In wine, electrical charges play a secondary role in colloidal stability, while macromolecular colloids as polysaccharides have the most important role. In fact, macromolecular colloids are known as “protective colloids.” This protective effect is attributed to a coating of the colloid particles that prevents them from agglomerating. When eliminating polysaccharides by adding enzymes, the system becomes unstable and colloids tend to flocculate. Therefore, wine clarification becomes easier to process. Different membrane materials exhibit different levels of adsorption of typical foulants in wine such as polysaccharides. Larger amounts of polysaccharides are adsorbed to PES than to PP membrane. PES membrane presents hydrophilic character while PP membrane has hydrophobic character. Polysaccharide and tannin

Membrane Fouling

► Fouling

adsorption take part in irreversible fouling of membranes during the crossflow microfiltration of wine. This adsorption is dependent on the membrane surface properties, especially its surface free energy. Polysaccharide adsorption is governed by membrane polarity: it decreased as surface polarity increased due to hydrophilic repulsion between surface and the hydrophilic macromolecules. Mannoproteins play a crucial role in reducing the permeate fluxes. Mannoproteins have the most pronounced fouling effect among the polysaccharides in wine. Their impact on the flow is dependent on their concentration. Phenolic compounds have a much more important affinity for membranes than the polysaccharides, and there are both quantitative and qualitative differences between the different materials. There is a direct relationship between membrane polarity and the amount of adsorbed or deposited polyphenols. The adsorption of polyphenols seems to be governed by two mechanisms depending on membrane material: polar interactions and hydrogen bonds. Polyphenol adsorption increased as the polarity and the basic component of the membrane surface free energy increased. The adsorption of wine tannins on membrane surface occurs in static conditions. Under dynamic conditions, the rate of fouling and its type is strongly influenced by the transmembrane pressure. The increase in irreversible fouling can be explained by the transition between the states of dispersed molecules to aggregates. This fact is promoted by the increase of the transmembrane pressure which forces the molecules to be near the membrane surface and promotes membrane/tannins and tannins/tannins interactions. Few data exists on the effect of wine proteins on membrane fouling. This is due to their elimination before filtration by fining. The large particles and microorganisms in crude wine are generally only implied in reversible fouling, while the removal of these particles did not modify the irreversible fouling. Numerous parameters influence fouling of membranes (initial wine, pressure, crossflow velocity, membrane material, etc.). Due to the type of fouling, no clear critical flux for irreversibility can be really determined for wine microfiltration.

Membrane Fouling Index

► [Fouling Index](#)

Membrane Function

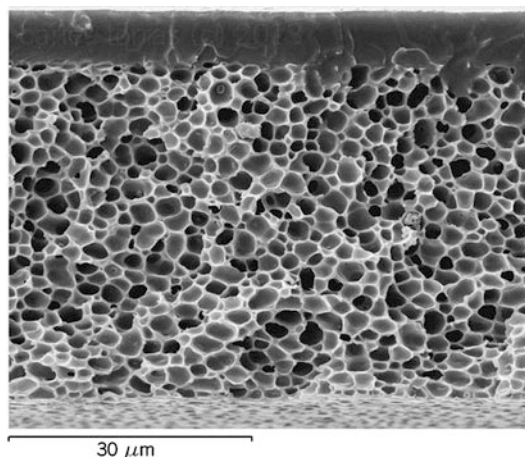
► [Membrane \(Definition, Function, Structure\)](#)

Membrane Micrograph

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Image is obtained from a membrane sample to acquire information regarding the morphology of the membrane (porous structure) (Torras et al. 2006). Nevertheless, it can also have other purposes, as characterized by fouling in the membrane (Saha et al. 2007). Typically, micrographs are two-dimensional images, although 3D reconstructions can be obtained by using advanced techniques (i.e., synchrotron) (Remigy et al. 2007). Equipment availability and characterization cost make 2D images to be the routine ones. Several apparatus can be used to obtain membrane micrographs: scanning electron microscopy, transmission electron microscopy, atomic force microscopy, etc. Due to typical sizes of membrane pores (from nanometers to hundreds of micrometers), scanning electron microscopy is, probably, the most versatile equipment. Nevertheless, if special attention is required in the nanometric range, atomic force microscopy may be the most suitable (phase and topographic images can be obtained) (Khulbe et al. 2008). Also, for large pore in sizes, optical microscopy can also be used. This last one is of special interest when used coupled with fluorescence, named confocal laser scanning microscopy (CLSM) (Ferrando et al. 2005). Nevertheless, for the last



Membrane Micrograph, Fig. 1 Polymeric membrane cross-sectional micrograph obtained by scanning electron microscopy

technique, the images can be named photographs since they are based on photons, while this last term cannot be used with electron microscopy, based on electron beams.

Two main types of 2D micrographs are obtained: surface and cross-sectional ones (Torras and Garcia-Valls 2004). Cross-sectional micrographs have the advantage to show the pore structure across all the membrane thickness (Fig. 1). In symmetric membranes (So et al. 1973), the pore size does not change in the mentioned direction, but it is usual that they do (asymmetric membranes), and in this last case, cross-sectional membranes are of special interest. Surface micrographs show the pore structure in a determined height of the membrane (considering height in the direction of the fluid flow, which is across the membrane). Usually, they correspond to the top and bottom side of the membrane. Surface micrographs let determine the regularity of the pores, check whether there is material deposited over the surface (a type of fouling), etc.

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Membrane Microreactor

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Today, several research groups are working on the development of novel apparatuses or methods that can dramatically decrease the equipment size to production capacity of various chemical processes. At the same time the objective is also to improve the energy efficiency of the plant with lower or no impact on the environment. This will finally lead to a cheaper and a more sustainable (more environmentally friendly) chemical process. This new trend in chemical process engineering is commonly named as “process intensification.” In general process intensification techniques can be categorized in two main streams: (1) process-intensifying equipment (e.g., static mixers, rotating devices, and microreactors) and (2) process-intensifying

methods (e.g., integration of reaction and separation in multifunctional reactor units such as in membrane reactors) (Stankiewicz and Moulijn 2000). Microreactors and membrane microreactors have the potential to be two key novel technologies for process intensification.

A microreactor is a device with size ranges of roughly 10–1000 μm (in length, width, height, and diameter) that is manufactured by means of precise engineering or microfabrication methods. Microreactors have several advantages and disadvantages in comparison with the conventional macroscale reactors. Microreactors are well known to outperform the conventional macroscale reactors in terms of heat and mass transfer characteristics (higher energy and material efficiencies). Also, microreactors are inherently safe to operate and normally have lower construction, operating, and maintenance costs in comparison with conventional macroscale reactors. At the same time microreactors have several disadvantages in compare with conventional devices. Clogging or fouling in microchannels, leakage between channels, and high fabrication cost of the reactor are the main drawbacks of going to microscale size range. Therefore, it is of paramount importance to select the most advantageous reactor type in each operating condition (Basile 2013).

A membrane reactor is a multifunctional device that integrates reaction and separation stages in one single unit and therefore enhances the efficiency of the process by reducing the number of steps. Membranes can be used to selectively remove components from the product stream to control the thermodynamic equilibrium of such a process (e.g., steam methane reforming). Also membranes can be applied to selectively add a reactant to the reaction zone to decrease the sharp increase in temperature at the presence of highly exothermic reaction. Therefore, integration of membranes to the reaction zone can enhance the efficiency of the process to higher degrees of process intensification.

The application of membranes to various chemical processes has been already investigated by several researchers (Basile 2013). Also microchannel reactors have been extensively

studied for the production of H_2 for fuel cell (via steam reforming, partial oxidation, water gas shift, and methanation reactions) (Hessel et al. 2009). Although a great interest has been paid on microreactors in the recent years, the application of membrane microreactors is still limited. Most of the literature on membrane reactors has been devoted on the production of H_2 using Pd-based membranes (Gallucci et al. 2013). More research needs to be devoted to the application and integration of membranes to microreactor devices.

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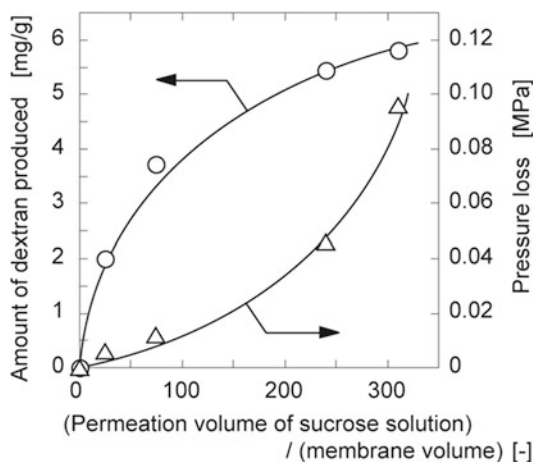
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Membrane Modification Using Dextran for Colloid Separation

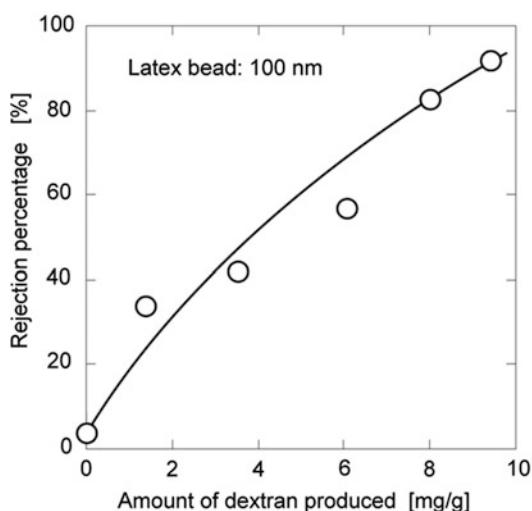
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Membrane modification using dextran for colloid separation (also called dextran-produced membrane) is the most interesting technique for the separation. Dextranase (DSase), a kind of transferase, produces dextran from sucrose. The produced dextran forms the complex with the active site of DSase. Dextran is α -(1,6) glucose



Membrane Modification Using Dextran for Colloid Separation, Fig. 1 Pressure loss of membranes and the amount of dextran produced in permeating sucrose solution through DSase-immobilized membrane (Kawakita et al. 2007)



Membrane Modification Using Dextran for Colloid Separation, Fig. 2 Rejection percentage of latex bead by the amount of dextran produced (Kawakita et al. 2009)

polymer and has the flexible structure. Up to now, dextran has been applied for separation and incubation materials. Using this property of DSase, we modified the surface of membrane pores with dextran. DSase was immobilized within the membrane pores by passing a DSase solution through a Shirasu porous glass inorganic porous hollow fiber membrane. The interaction between DSase and membrane surface would be hydrophilic interaction. Via the interaction, the structure of DSase was not destroyed. Subsequently, a sucrose solution was passed through the DSase-immobilized membrane to generate dextran. In permeating sucrose solution, the produced dextran occupied the inner part of the membrane, because dextran is produced from the active site of DSase. The transmembrane pressure drop during solution permeation increased with increasing dextran production (Kawakita et al. 2007), as shown in Fig. 1. The porosity of the membrane filled with dextran was quantitatively determined from the pressure loss using the Kozeny-Carman equation. A colloidal particle suspension was passed through the dextran-modified membrane, showing rejection of the colloid particles by the dextran (Kawakita et al. 2007), as shown in Fig. 2. In methanol solution, dextran shrinks because the

hydrated water leaves from dextran. In permeating methanol/water solution through dextran-produced membrane, the pressure drop increased due to the shrinkage of dextran polymer. Next, the dynamic separation of colloidal particle was performed; colloidal particles were separated by the dynamically produced dextran. A colloidal particle suspension containing sucrose was also passed through a DSase-immobilized membrane, demonstrating that the colloidal particles were dynamically rejected during dextran generation (Kawakita et al. 2009). If DSase could be immobilized on polymeric materials, dextran with controllable hydrophilic characteristics could be generated by changing the density and the length of the chains.

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Membrane Morphology

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Synonyms

Surface morphology

Surface membrane morphology studies provide atomic or nano-scale structure information about pore shape, pore size distribution, roughness, electrical properties, surface adhesion/membrane fouling behavior, and correlation between membrane characteristics and process behavior.

Analytical Imaging Techniques used for surface morphology study include

- Field Emission Scanning Electron Microscopy (FE-SEM)
- Focused Ion Beam – Scanning Electron Microscopy (FIB-SEM)
- High Resolution Optical Microscopy
- Scanning Transmission Electron Microscopy (STEM)
- Transmission Electron Microscopy (TEM)
- Ultra High Resolution-SEM (UHR-SEM)
- Atomic force microscopy (AFM)

These methods provide high-spatial-resolution images that show the relative surface morphology of membrane structure.

Atomic force microscopy has proved to be a powerful technique to study membrane morphology. It can magnify up to $\times 1,000,000$ in 3D view and can give important quantitative data analysis (including sizes, surface roughness, and area) about membrane surface in air or in liquid medium. Materials investigated using AFM include thick and thin film coating, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors (Khulbe et al. 2008; Hilal et al. 2012).

Although still controversial, there are some indications that correlate the process performance with the surface roughness. Irregularities on the membrane surface may affect the physicochemical properties of the membrane. The behavior strongly depends on the type of materials and method of membrane preparation. For example, it has been shown that for gas separation through poly(phenylene) oxide (PPO) membranes, permeability increases while selectivity decreases with an increase of surface roughness.

In pervaporation of water/ethanol mixtures through aromatic polyamide with acrylamide grafted by plasma polymerization, both separation factor and permeation rate increased linearly with roughness. In reverse osmosis membranes fouling seems to increase with surface roughness.

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Membrane Operations

- [Food Packaging, Membranes for](#)

Membrane Preparation Techniques

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Membrane technology is nowadays more and more employed in many separation processes such as water desalting and blood purification, to

mention two of the most known. Synthetic membranes can be prepared according to several techniques which allow to forge a material so as to give it the desired characteristics, the most important of which is the *morphology* (Mulder 1996; Baker 2004). In order to prepare membranes for a given separation, two aspects must be considered: the nature of the used material (organic or inorganic) and the morphology (dense or porous) of the membrane. In the table below, the most important techniques are reported together with salient features.

Sintering is a technique which allows to prepare membranes from powders of polymeric materials such as polyethylene (PE) and polypropylene (PP) or of inorganic materials such as stainless steel, metal oxides, graphite, or glass. This technique is based on the compression of the particles of the selected material and heating to a temperature below the *melting point* so as to induce a sticking of the particles. Between the stuck particles, *pores* are formed the size of which strictly depends on the particle size: the smaller the particle size, the smaller the pore size. The SEM micrograph of a stainless steel sintered membrane is shown in Table 1 (a). Sintered membranes are particularly suitable for applications in harsh conditions owing to the great resistance of the based materials in chemically aggressive environment or at high temperature. Polytetrafluoroethylene (PTFE), further to these outstanding properties, also exhibits high flexibility which makes it particularly suitable as membrane material.

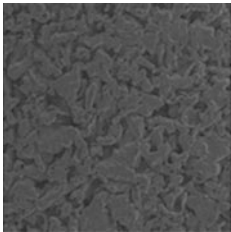
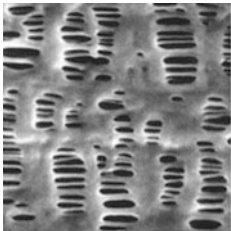
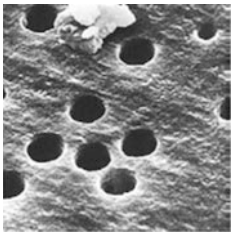
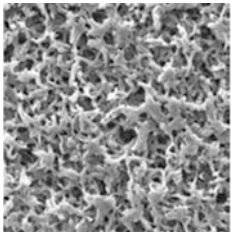
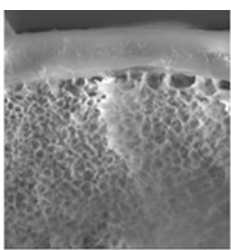
Stretching technique is used to prepare porous membranes starting from extruded dense films of *semicrystalline* polymers such as PE, PP, and PTFE. Pore formation is obtained by stretching the film perpendicularly to the direction of extrusion until small ruptures occur in the structure of the dense film (SEM image (b) in Table 1). Pore size of membranes prepared by this technique (0.1–3 μm) makes them suitable for *microfiltration* applications. The *porosity* of the stretched membranes, given by the ratio of the void volume and the total volume of the membrane, may also reach 90 %.

Differently from all the others, membranes prepared by **track-etching** technique present uniform pores with cylindrical geometry (SEM image (c) in Table 1). The principle of the technique is the irradiation of a dense film of polymer, usually polyester or polycarbonate. The radiation crosses the film perpendicularly to the surface and damages polymer chains encountered along the path. A subsequent chemical treatment, typically with NaOH, removes the damaged material creating straight cylindrical pores. The number of pores and their size is determined by the exposure time to the radiation and to the etching treatment, respectively. A drawback of this technique is the rather low porosity of the membranes, ranging from 5 % to 10 %.

Phase inversion. This is the most versatile technique which allows the preparation of all kinds of membranes. Only polymeric membranes can be prepared, provided that the polymer is soluble in a solvent. According to this technique, a polymer dissolved in a solvent passes from the fluid state to the solid state under controlled conditions to give rise to the formation of membranes. The control of the operating conditions is crucial in order to prepare membranes with the desired morphology. The rate of removal of the solvent and the velocity of the phase separation are the most important steps which mainly determine the morphology of the membranes. With this technique it is possible to prepare membranes both in flat and in tubular conformation with morphology ranging from dense to microporous (SEM image (d) in Table 1).

Solution coatings. This technique allows the preparation of *composite membranes*, the use of which is desirable when the separation to be accomplished is controlled by the *diffusion* rather than by the size of the species to be separated. Membranes prepared with this technique are formed by two different materials the first of which is a thin dense film made of a selective polymer deposited on top of the second one which merely acts as a porous support. The SEM image (e) in Table 1 shows the cross section of a composite membrane. Such a conformation increases the transport rate through the membrane thanks to the thinness of the dense layer, while the

Membrane Preparation Techniques, Table 1 Membrane preparation techniques. SEM images (b), (c) and (d) reprinted from “Membrane Technology and Applications” 2nd edn. by Richard W. Baker with permission from John Wiley & Sons Ltd.

Techniques	Materials	Pore size (μm)	Field of applications	Morphology (SEM image)
Sintering	Powders of polymers, metals, ceramics, graphite	0.1–10	Microfiltration	 (a)
Stretching	Semicrystalline polymers	0.1–3	Microfiltration	 (b)
Track-etching	Thermoplastic polymers	0.02–10	Ultrafiltration, microfiltration	 (c)
Phase inversion	Polymer solutions	From dense to few microns	All fields	 (d)
Solution coatings	Polymer solutions	Dense	Nanofiltration/gas separation	 (e)

porous support ensures mechanical stability. *Dip coating, spray coating, spin coating, and plasma polymerization* are some of the procedures for preparing composite membranes.

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Membrane Pretreatment

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Membrane pretreatment refers to the series of source water conditioning processes in reverse osmosis desalination plants performed using membranes.

The polymeric thin film composite membranes used in reverse osmosis desalination plants require extensive pretreatment of the source water due to their structural limitations. Pretreatment steps include the removal of particulate, organic foulants, and, in some cases, chlorine. Conventional pretreatment technologies include granular media filtration using multiple layers of granular media (e.g., sand or anthracite) in single- or dual-stage configurations. These will not be covered further here. Membrane pretreatment is based on a combination of microfiltration (MF) and ultrafiltration (UF) and can be further classified according to the driving force, either pressure or vacuum if submerged.

Membrane pretreatment is becoming the dominant pretreatment method for RO plants with some of the largest installations in the world adopting it to replace conventional granular media (Gasia-Bruch et al. 2011). These include the Perth II plant (300,000 m³/day) in Australia

and the Shuwaikh plant (350,000 m³/day) in Kuwait (Gasia-Bruch et al. 2011).

The types of membranes and operating parameters for the pretreatment stage are linked to those of the RO membranes and the characteristics of the source water feed (pH, temperature, conductivity, turbidity, dissolved gases, particulates, etc.). Regarding the former, a common measure used in industry for the initial design of RO plants is the fouling index of RO membranes. This is based on a simple testing of the RO membrane using a feed containing a known amount of suspended or colloidal particles. The result is a numerical value that provides a relative estimate of fouling. The modified fouling index is a refinement of the previous one and is capable of discriminating the type of fouling mechanism occurring (e.g., pore blocking, cake filtration, etc.) (Schippers and Verdouw 1980). The initial design is then further optimized by coupling process parameters such as flux and transmembrane pressure between the pretreatment and the RO stages. Both dead-end and cross-flow are used in industry, with the former having lower footprint and energy costs but requiring intermittent operation to remove the accumulated solids and the latter capable of operating continuously but requiring a larger footprint due to lower packing density and higher energy costs due to the requirement of maintaining the tangential flow.

All membrane pretreatment installations have four basic modes of operation: filtration, backwash, cleaning, and integrity testing.

The flow direction is periodically reversed to remove accumulated solids on the feed side, a process known as backwash. Filtered water, concentrate, and air are all used, often in combination, with the objective of minimizing the backwash time while at the same time maximizing the removal of solids. Over time, membranes in the pretreatment stage require stronger chemical cleansing to remove biofilm and organic fouling. This process, often called maintenance wash, requires the removal of individual membranes from the line.

Backwash and maintenance wash do not remove completely membrane fouling, and a more extensive cleaning is required. Timing of this longer process varies with the feed quality as is generally triggered by a set reduction in the transmembrane pressure. Typical chemical cleansing includes recirculation of low pH solutions followed by high pH ones.

Polyamide RO membranes require the removal of all excess chlorine present in both maintenance wash and cleaning stages. Common methods include using a chlorine scavenger, such as sodium hydrogen sulfite, or sorbents such as activated carbon. The former method is more economic in terms of both capital and running costs and is generally preferred. Alternatively sodium hydroxide can be used to replace chlorine-based cleaning agents.

Integrity testing is performed periodically on pretreatment membranes to detect punctures or ruptures in the membranes. The most commonly used off-line test is the so-called pressure hold test, whereby air is forced through the membrane module at a certain pressure, the circuit closed, and loss over time is monitored. In-line testing is commonly based on monitoring changes in turbidity after each membrane module compared to the average turbidity of the whole train.

Cross-References

► [Polyamide \(PA\)](#)

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Membrane Reactor Equilibrium Conversion

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The equilibrium constant of any reaction is function of temperature only. The equilibrium of a conventional/traditional reacting system is function only of the thermodynamic variables (temperature, pressure, and mixture composition). It is independent from the reactor model (continuous stirred tank reactor, plug flow reactor, batch reactor, etc.), fluid dynamics (mixing, diffusion, etc.), heat exchange (isothermal, adiabatic, or no-isothermal reactor), reactor size, etc. since the equilibrium is reached when variation in temperature, pressure, and composition is no longer present in the chemical system.

This condition is mathematically expressed by the following equations set valid for a reacting closed (no mass transfer with the environment) system consisting of N reactions.

$$Kp_j = \prod_{i=1}^{N^{\text{Gas}}} [P^{\text{Reaction}} x_i(X_1, X_2, \dots, X_N)]^{v_{ij}} \quad (1)$$

$$j = 1, \dots, N^{\text{Reaction}}$$

The formulation in terms of Kp constants enables for the evaluation of reaction conversion and hence the equilibrium composition of the reacting system kept under a set reaction pressure. As well known, the equilibrium expresses the highest limit for reaction conversion, and it will be here indicated as **TREC** (Traditional Reactor Equilibrium Conversion).

The conversion of a real chemical reactor (of finite size) depends on several factors, e.g., reactor model, feed flow rate, residence time, and heat transfer with the environment in addition to the variables before indicated. Thus, its conversion is always lower than the equilibrium one.

A membrane reactor (MR) has, in addition to the traditional reactor, another chamber/volume: the one named permeate. Therefore, it consists of two (reaction and permeation) volumes separated by a selective membrane. One can image each chamber is provided with a piston moving without friction, for keeping a constant pressure; consequently, the reaction and permeation volumes change according to the pistons movement. In addition, the reaction pressure can be different from the permeate pressure. During the reaction, the chamber volumes change for achieving the chemical and permeating equilibria. As the reactive equilibrium, the permeative one has a dynamic character such as the reactive one; this means molecules (if any) permeating the

membrane from reaction side to permeate side are equal in number to the molecules permeating in the opposite direction.

Temperature, pressure, and composition of the permeate can be different from those of reaction volume. These variables have also to be taken into account for evaluating the equilibrium of an MR. Nevertheless, another constrain is required for the equilibrium of an MR in addition to the one defined by Eq. 1 for the traditional reactor. This is the permeation equilibrium expressed as the equality of the chemical potentials (e.g., partial pressures for a gas phase reaction) (Barbieri et al. 2001, 2005; Marigliano et al. 2003) on both membrane sides of any permeable species Eq. 2.

$$\begin{aligned} \text{ChemicalPotential}_i^{\text{Equilibrium}} &= \text{ChemicalPotential}_i^{\text{Reaction}} = \text{ChemicalPotential}_i^{\text{Permeation}} \\ \text{Pressure}_i^{\text{Equilibrium}} &= \text{Pressure}_i^{\text{Reaction}} = \text{Pressure}_i^{\text{Permeation}} \end{aligned} \quad (2)$$

$\forall$ permeable species

This condition is independent from the membrane type and permeation rate. As chemical equilibrium in a conventional reactor, and in an MR as well, is independent from the reaction path, similarly the MR equilibrium is independent from permeation rate.

The hydrogen permeates Pd-based membranes following the Sieverts law. Even though, the membrane characteristics (e.g., Pd, Pd-Ag, thickness, etc.) influence the permeation rate and hence the time necessary to reach the equilibrium, the value of these parameters does not affect the MR equilibrium.

The equilibrium depends on the extraction capacity of the membrane system which is a function of the temperature, pressure, and composition of the MR permeate volume that directly gives the condition of Eq. 2.

The **MREC** (Membrane Reactor Equilibrium Conversion) can be easily calculated using the constrains of Eqs. 1 and 2. MREC can be also calculated using the thermodynamics table for the reaction(s) adding to it the terms related to the permeative equilibrium.

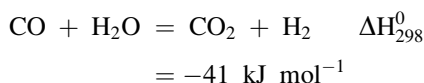


Table 1 reports the thermodynamics table for calculating the equilibrium conversion of the water gas shift reaction in a Pd-based MR, all the figures are in moles. The procedure for calculating the number of moles at the equilibrium is the one known since long time from chemistry as the fourth row “reactive equilibrium state” of Table 1 shows. In fact, in absence of a membrane this conversion is the one of a traditional reactor and here is identified as TREC. The presence of a selective membrane contributes to product (hydrogen) removal and hence to increase the equilibrium conversion because of the mass law effect or the Le Châtelier–Braun principle. Therefore, the equilibrium conversion of a reactor conversion (here named MREC) is always higher than TREC. MREC is equal to TREC in absence of any permeation.

Membrane Reactor Equilibrium Conversion, Table 1 Thermodynamics table for water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) in an MR. Both reaction and permeating equilibrium are taken into account

Reaction	CO	H ₂ O	CO ₂	H ₂
Initial state	n_0	$m n_0$	$m_1 n_0$	$m_2 n_0$
Reaction conversion	$-x n_0$	$-x n_0$	$x n_0$	$x n_0$
Reactive equilibrium state	$n_0 (1-x)$	$n_0 (m-x)$	$n_0 (m_1 + x)$	$n_0 (m_2 + x)$
Permeation	—	—	—	$-z [n_0 (m_2 + x)]$
Reactive and permeative equilibrium state	$n_0 (1-x)$	$n_0 (m-x)$	$n_0 (m_1 + x)$	$n_0 [(m_2 + x) (1-z)]$
Total mole number	$n_0 [1 + m + m_1 + m_2 - z (m_2 + x)]$			

Where, $m > =x$; $x = \text{MREC}$; z permeate hydrogen fraction
 m , m_1 , and m_2 are the feed molar ratio with respect to CO of H₂O, CO₂, and H₂, respectively

The fifth row includes the term (z) for hydrogen permeation through a Pd-based membrane, whereas the sixth row reports the moles present in the reaction volume under the reactive and permeative equilibrium condition.

The total mole number in an MR owing to permeation is lowered by the reducing term $\{-z [n_0 (m_2 + x)]\}$ with respect to traditional reactor.

The equilibrium constant of the reaction (reactive constrain, see Eq. 1) for WGS reaction considering the reactive and permeative equilibrium terms can be expressed as

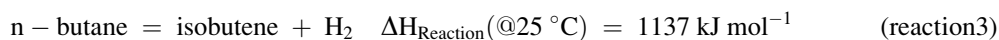
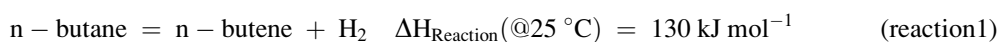
$$K_P = \frac{(m_1 + x)[(m_2 + x)(1 - z)]}{(1 - x)(m - x)}$$

The other, permeative constrain Eq. 2 for the hydrogen, the only permeating species is

$$P_{H_2}^{\text{Equilibrium}} = \frac{n_0 [(m_2 + x)(1 - z)]}{n_0 [1 + m + m_1 + m_2 - z(m_2 + x)]} P^{\text{Reaction}}$$

CO conversion and the hydrogen fraction permeate the membrane are calculated resolving this set of two equation in two unknowns: the conversion (MREC) and the hydrogen permeated the membrane.

Another example of using thermodynamics table is reported for the n-butane dehydroisomerization (Al-Megren et al. 2013). This reaction (reaction 3) involves the dehydrogenation of n-butane (reaction 1) and successive isomerization to isobutene (reaction 2). The main products measured were normal butenes, isobutane, and isobutene.



From the thermodynamics table (Table 2), after some algebra, the equilibrium constants for reaction 1 and reaction 2 and the permeation equilibrium condition are:

$$K_{P1} = \frac{x^2(1-z)(1-w)}{(1+x-xz)(1-x)} P^{\text{Reaction side}}$$

$$K_{P2} = \frac{w}{(1-w)}$$

$$P_{\text{hydrogen}}^{\text{Equilibrium}} = P^{\text{Reaction side}} \frac{x(1-z)}{(1+x-xz)}$$

This is a set of three equation in three unknowns that resolved for x , w , and z gives the conversion

Membrane Reactor Equilibrium Conversion, Table 2 Number of moles determination at reactive and permeative equilibrium in a membrane reactor

Moles	n-butane	n-butene	Isobutene	Hydrogen
Initial state	n_0	—	—	—
Reactive state of reaction 1	— $n_0 x$	$n_0 x$	—	$n_0 x$
Reactive state of reaction 2		— $n_0 x w$	$n_0 x w$	
Permeation state	—	—	—	— $n_0 x z$
Permeative and reactive equilibrium state	$n_0 (1 - x)$	$n_0 x (1 - w)$	$n_0 x w$	$n_0 x (1 - z)$
Total number of moles				$n_0 (1 + x - xz)$

Where, x = MREC for [reaction 1](#), w = MREC for [reaction 2](#), z permeate hydrogen fraction
The initial concentration of n-butene, isobutene, and hydrogen was chosen as zero

values (MRECs) of the [reaction 1](#) and [reaction 2](#) and the permeate hydrogen fraction.

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important role in determining how the membrane surface will interact with its environment. For example, surface roughness is important in evaluating the performance of a membrane as it may influence the transmembrane transport and fouling potential of the membrane (Hobbs et al. 2006). The surface roughness may also correlate with other material characteristics such as the pore-size distribution and molecular weight cutoff (Bowen and Doneva 2000). Membrane roughness is usually quantified by one or more of a range of parameters. The most common parameters used are:

- (i) Peak-to-valley roughness
The peak-to-valley roughness describes the maximum observed range in a sample area and is given by the distance between the highest peak ($Z_{\max}$) and the lowest valley ($Z_{\min}$) on the measured surface, where Z indicates the vertical height of the surface:

$$R_{pv} = Z_{\max} - Z_{\min}$$

- (ii) Average roughness
The average roughness (R_a) is the most widely used because it is a simple parameter to obtain when compared to others. The average roughness is calculated using

$$R_a = \sum_{n=1}^N \frac{|Z_n - \bar{Z}|}{N}$$

where Z_n is the height at sample point n , $\bar{Z}$ is the height of the center plane, and N is the total number of points in the sample area.

Membrane Roughness

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Membrane Roughness: Surface roughness is a measure of the texture of a surface. For membranes, the roughness may be defined as the deviation of the actual membrane surface topography from an ideal atomically smooth surface. Roughness plays an

(iii) Root-mean-squared roughness.

The root-mean-squared roughness (R_{RMS}) is a statistical measure used in many different fields. The R_{RMS} value is given by the standard deviation of the Z values for the sample area:

$$R_{RMS} = \sqrt{\sum_{n=1}^N \frac{(Z_n - \bar{Z})^2}{N}}$$

The RMS roughness of a surface is similar to the average roughness, with the only difference being in the use of the mean-squared absolute values of the surface roughness profile. As the RMS roughness contains square terms, large deviations from the average height are weighted more heavily than for the mean roughness.

Experimental determination of the membrane surface roughness is almost always conducted using atomic force microscopy (AFM). However, there is some difficulty when comparing results reported in literature due to the variation in the methods applied and the sample areas examined (Boussu et al. 2005).

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Membrane Rugosity

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Membrane Rugosity: Membrane rugosity is a measure of small-scale variations or amplitude in

the height of a surface. The rugosity (or roughness factor) of a surface, f_r , is calculated using the ratio (IUPAC et al. 1997):

$$f_r = \frac{A_r}{A_g}$$

where A_r is the real (actual) surface area and A_g is the geometric surface area.

Membrane rugosity is synonymous with membrane roughness (see entry on ► [membrane roughness](#)).

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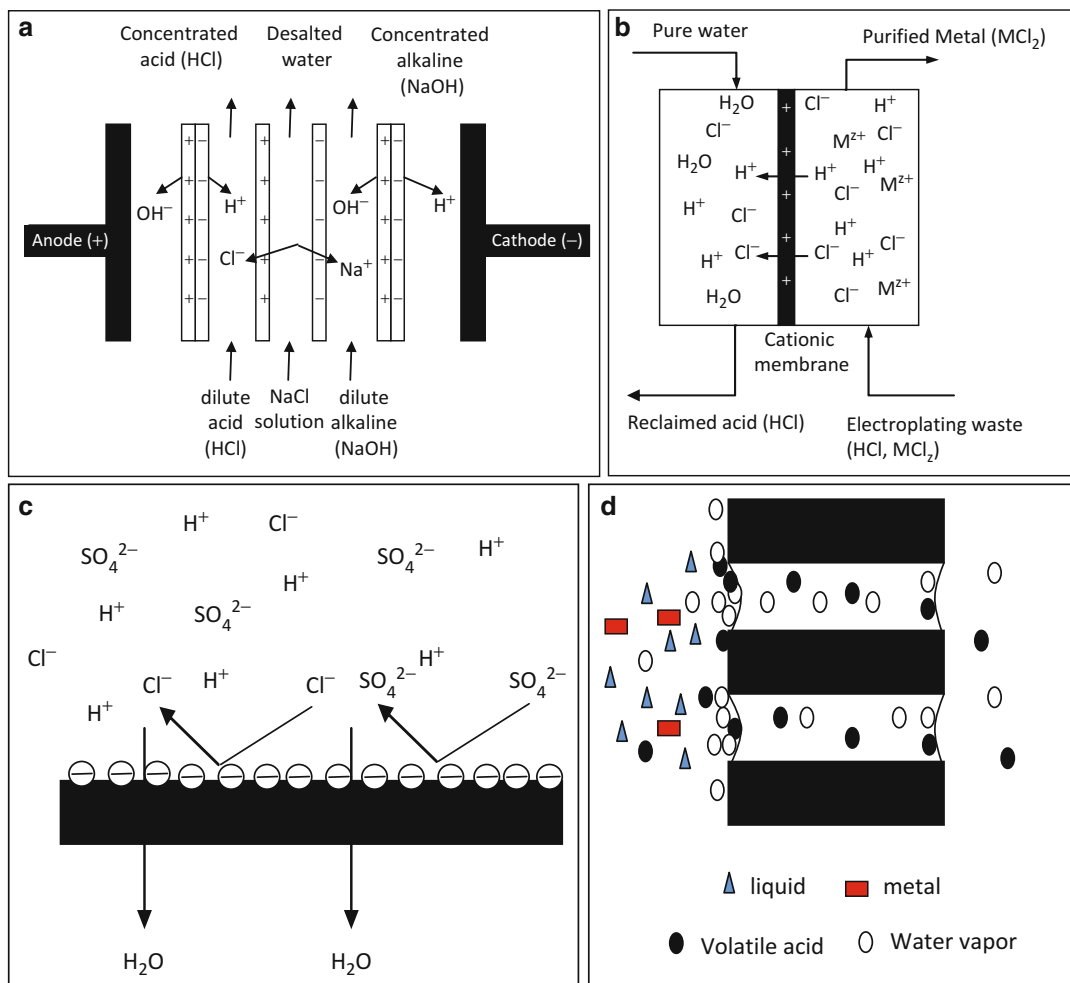
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Membrane Separation of Inorganic Acids

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Membrane technology plays a particular role in acid recovery through their specific separation mechanisms. Membrane processes in mode of electrodialysis, diffusion dialysis, nanofiltration/reverse osmosis, and membrane distillation system are commonly employed. Their role as clean technologies reuses acids as valuable materials and therefore contributes to reduction of the environmental load.

Electrodialysis (ED) has been used for the recovery and recycling of dilute waste acid. Electrodialysis is used to transport salt from the diluate to the concentrate by applying an electric current. The ions are transported through semipermeable membrane, under the influence of an electric potential. Cation-selective membranes are negatively charged matter, which rejects negatively charged ions and allows positively charged ions



Membrane Separation of Inorganic Acids, Fig. 1 (a) Bipolar electrodialysis, (b) chemo-dialysis, (c) reverse osmosis/nanofiltration, (d) membrane distillation

(Na^+ , H^+) to flow through, whereas anion-selective membranes will allow negatively charged ions (Cl^- , OH^-) to permeate. The separation mechanism of ED is shown in Fig. 1a. ED was able to concentrate the acid by a factor of 2–3 (up to concentration of 1.0 M). Available ion exchange membranes used in electrodialysis applications include Neosepta[®], Selemiom[®], Aciplex[®], Nafion[®], and Ionac[®]. A short-term test using membrane Raipore 6030 from Pall shows that the energy requirement can be as low as $1.41 \text{ kW.h.kg}^{-1}$ and maximum achievable of 80 % nitric acid in anolyte (Ponce-de-León and Field 2000).

A process of chemo-dialysis (CD) using a chemically active membrane material such as poly(benzimidazole) has been proposed for the transport of inorganic acids. Acids are transported across the membrane by concentration gradient as the driving force. The transported acid molecules are stripped away from the permeate side by a suitable stripping agent. These membranes show appreciable transport rates for H_2SO_4 , HCl , and HNO_3 with the fluxes for different acids varied from 15 to $140 \text{ g/m}^2 \text{ h}$ under different operating conditions. CD with high selectivity towards noncharged solute eliminated the requirement of acid neutralization, thus this process is

economically attractive. The schematic diagram of CD is shown in Fig. 1b.

The coupling reverse osmosis (RO) and nanofiltration (NF) are effective methods that could replace the conventional extraction method for acid recovery. Both RO and NF are pressure driven process which allows the uncharged water molecules to pass through but retain the charged acid molecules through size and charge exclusion (Fig. 1c). Stability of the membrane under such a low pH is always a concerning issue.

Recently, membrane distillation (MD) was suggested for the regeneration of volatile inorganic acids from the metal pickling solutions using hydrophobic porous and nonporous asymmetric membranes. Membrane distillation is a thermally driven separation process in which separation is enabled due to phase change or vapor pressure difference between feed and permeate (Fig. 1d). It was shown that the concentrating of volatile inorganic acids in the feed using a porous tetrafluoroethylene/vinylidene fluoride copolymer (MFF-2) membrane is effective up to 1.0 N concentration (Elkina et al. 2013).

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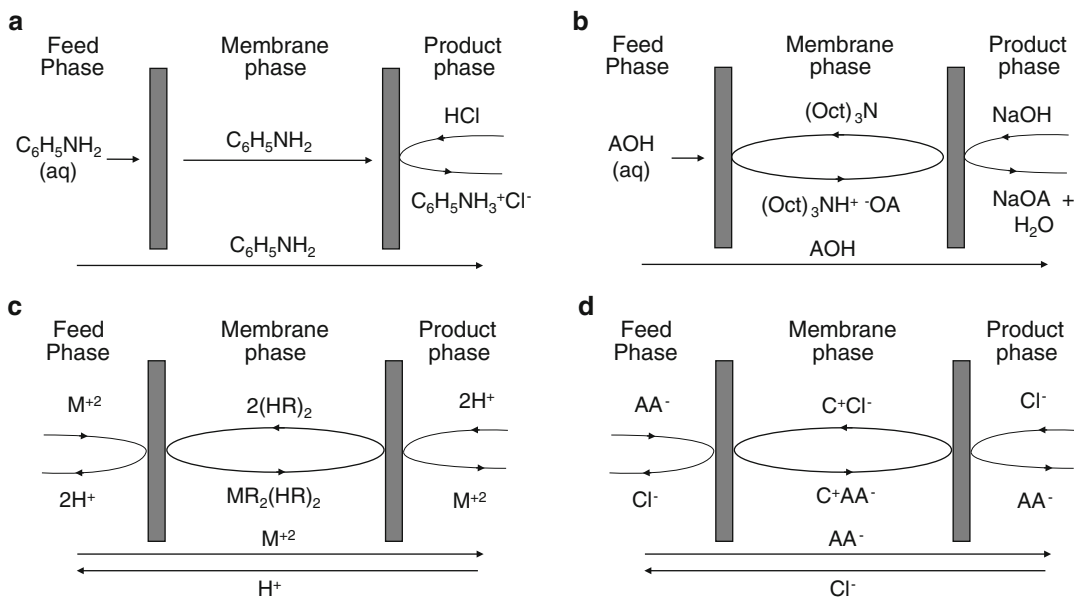
Membrane Stripping

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Membrane stripping (synonym: membrane releasing) is a process to release in the product phase of a liquid membrane a target specie, which has been

transported through the membrane phase alone or complexed with a carrier, by the reaction, in the membrane phase/product phase interface, with a chemical specie or stripping agent added to the product phase. A liquid membrane is a system that involves a liquid (membrane phase), immiscible with the source solution (feed phase) and with the receiving solution (product phase), which serves as a semipermeable barrier between those two phases. The target specie can be transported from the feed to the product phase by dissolving in the membrane phase and diffusing to the product phase due to the concentration gradient between these two phases. It can also be done by forming (in the interface feed phase/membrane phase) with a carrier compound, added to the membrane phase, a reversible complex which is transported through the membrane phase due to its concentration gradient and broken (in the membrane phase/product phase interface), liberating the target specie in the product phase. In both cases, the process ends when the concentration of the target specie equalizes on both sides of the membrane phase. In order to improve the effectiveness of the liquid membrane separation processes, by maximizing both the extraction velocity (flux through the membrane phase) and the reception capacity of the diffusing specie in the product phase, a stripping agent is added to the product phase to release the target specie in that phase. The membrane stripping process occurs in the membrane phase/product phase interface in two ways. The first is by direct reaction of the stripping agent with the target specie; this gives rise to a membrane insoluble product that prevents it from diffusing back through the membrane (type I facilitation) (Fig. 1a). The other way is by reaction of the stripping agent with complex carrier-target specie, breaking that complex, removing the target specie from that complex, releasing it in the product phase, by formation (Fig. 1b) or not (Fig. 1c, d), with the stripping agent, the insoluble compound in the membrane phase, and regenerating the carrier, which initiates a new transportation cycle (facilitated transport type II) (Chakraborty et al. 2010; Vitt et al. 2010).

When the reaction between the diffusing specie and the stripping agent leads to a membrane



Membrane Stripping, Fig. 1 Membrane stripping of (a) an organic base by HCl; (b) an organic acid/carrier complex by NaOH; (c) a metallic ion/carrier complex by protons; (d) an amino acid/carrier complex by chloride ion

insoluble product, the driving force for the transport is generated by the concentration gradient of the target specie across the membrane phase due to the reduction to zero of its concentration in the product phase. When the reaction between the stripping agent and the target specie-carrier releases the target specie in its original form, the driving force for the transport of the target specie is maintained by a concentration gradient of a second specie transported in the opposite direction. Different types of membrane stripping processes can be used, but they should all be quantitative and very fast. The choice of a specific membrane stripping process should be determined by the nature of the target specie to be removed and recovered and by the nature of the carrier, if carrier-mediated transport is used. In this case, the selection of the carrier/stripping agent system is based on thermodynamic and kinetic considerations (Gu et al. 1992). Thermodynamically, the selected carrier should favor the formation of its complex with the target specie in the feed/membrane interface and its rupture in the membrane/product interface. Kinetically, the

selected carrier/stripping agent system should exhibit fast reactions for both extraction and stripping processes.

Cross-References

► [Stripping Agents: Use in Liquid Membrane System](#)

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Membrane Swelling

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Slow diffusion of solvents into polymer chains causes a swelling phenomenon and leads to a swollen polymeric membrane (Fig. 1). In this case, an expansion of the polymer network is promoted because polymer-polymer interactions are over polymer-solvent forces and a complete dissolution of the membrane is prevented (Billmeyer 1984).

Different degrees of swelling can be achieved depending on cross-linking, crystallinity, as well as intermolecular forces involved. The choice of the materials and their combination can direct the swelling events and make the membrane performance addressable at macroscopic level (Barton 1983). Membrane swelling over an area of 1 mm² is indicated as a bulk swelling, while small changes in dimension are classified as a microscopic swelling and are detectable by small-angle X-ray scattering (SAXS).

The macroscopic swelling is usually calculated by gravimetric measurements according to this relation:

$$G(\cdot/\cdot) = \frac{m - m_0}{m_0} \cdot 100 \quad (1)$$

where G is the percentage of swelling, m the mass of the wet membrane, and m_0 the mass of the dry membrane. The gravimetric method is, however, somewhat limited and inadequate when slow

anisotropic swelling equilibrium is reached or swelling kinetics need to be detected in real-time. In this case, in situ detection of the dimensional membrane is requested when moving from dry to wet state (Izak et al. 2007).

Robust network architectures of swelled membranes with high surface-to-volume ratio are generated when swelling takes place along three directions, x , y , and z . This physical expansion can be estimated by using the following relation:

$$\tau(\cdot/\cdot) = \frac{l - l_0}{l_0} \cdot 100 \quad (2)$$

where τ is the percentage of the membrane dimension; l the dimension of the wet membrane along the x , y , or z axis; and l_0 the dimension of dry membrane along the considered axis (Gugliuzza and Drioli 2007). The swelling can be isotropic when the expansion is equal in all directions, whereas differential dimensional changes in the plane (x , y) or along the vertical axis (z) to the plane lead to an anisotropic swelling (Fig. 2).

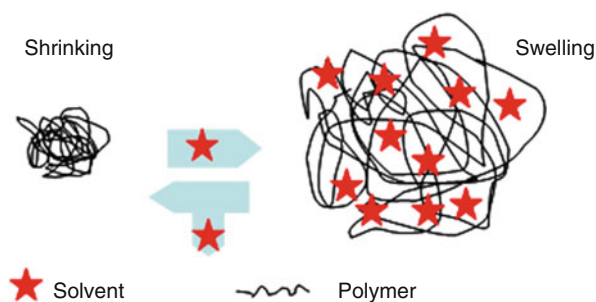
Reversible swelling is called as a deswelling. The cycle of swelling-deswelling is a mechanical work, which is often used in actuation and biosensing and drug delivery. In this case, switching swollen polymers are indicated as smart gels (Diaconu et al. 2012).

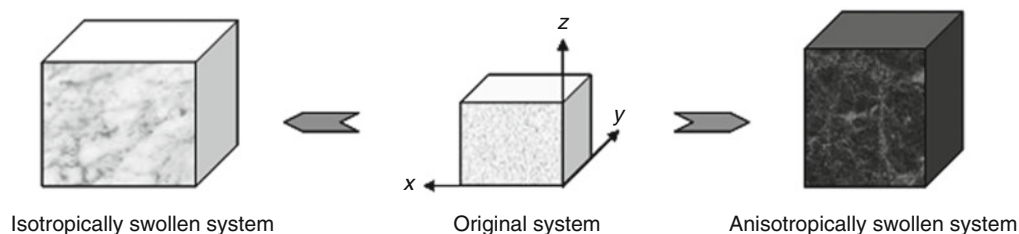
In dense membranes, a large sorption of molecules can induce swelling of the matrix leading to an increase in free volume. Higher mobility of the polymer chains reduces the discriminating power of the membrane, causing plasticization when macroscopic segmental motion occurs. In porous membranes, macroscopic swelling could lead to

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Membrane Swelling,

Fig. 1 Reversible expansion and shrinking of polymer chains after solvent adsorption/desorption



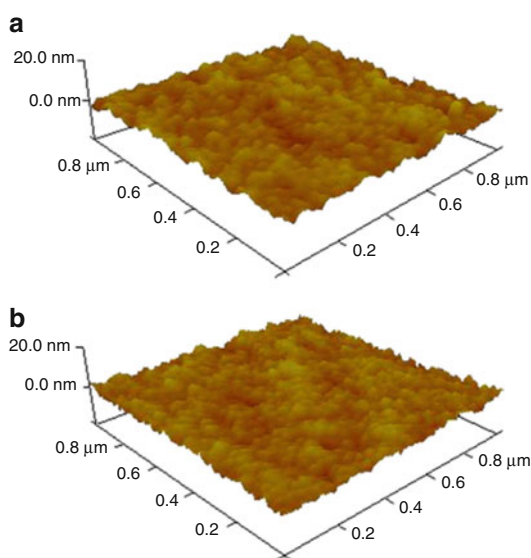


Membrane Swelling, Fig. 2 Isotropic and anisotropic expansion of 3D polymeric networks along three axes (x , y , and z)

an increase in the polymer volume with closure of porous structures and subsequent abatement of the flux.

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Membrane Topography, Fig. 1 The three-dimensional images of membranes by AFM. (a) A6DT and (b) PA6DT-C (Cheng et al. 2011)

Membrane Topography

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Membrane topography: At the nanoscale membranes are not flat surfaces. Membrane topography is concerned with the study of the membrane surface shape and features. In a broader sense, membrane topography is concerned with detail in general about membrane surfaces. Some of the more popular surface characterization techniques for membrane topography include

scanning electron microscopy (SEM) and atomic force microscopy (AFM). Each of these tools is capable of providing atomic-level quantitative analyses of the morphological characteristics of membrane surfaces. Using these tools, it is possible to characterize membrane properties like surface roughness, porosity, and pore size distribution (Bowen and Hilal 2009; Barbosa and Silva 2012) (Fig. 1).

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Membrane Use in Biodiesel Production from Microalgae

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In biodiesel production from microalgae, membrane separation can play an important role in process intensification and product purification. Membrane technology can be easily integrated into various steps of biodiesel production: harvesting and dewatering of microalgae and purification of triacylglycerols from wet microalgae for biodiesel production.

Algal biomass harvesting refers to the process of concentrating a diluted microalgae broth (<1 wt%) to a slurry or solid paste containing 5–25 % wt, or more, total suspended solids (Grimaa et al. 2003). Algal biomass harvesting is a significant challenge in microalgae production, due to the unique physical properties of microalgae, including the small size (3–30 μm) of microalgae cells and a density comparable to water. The cost for algal biomass harvesting accounts for 20–30 % of the operational cost of microalgae production (Grimaa et al. 2003). Among various techniques (gravity sedimentation, centrifugation, filtration, flocculation, flotation, electron-coagulation) used for microalgae harvesting, membrane filtration has many advantages, including the high separation efficiency, low energy cost, operational simplicity, and reduced chemical addition. In microalgae harvesting, both pressure and vacuum filter are promising filtration technologies. For relatively

larger microalgae cells, such as *Coelastrum proboscideum* and *Spirulina platensis*, both pressure and vacuum filter can achieve excellent filtration performance (Mohn 1980). In a pressure filter, a concentration factor of 245 was achieved in batch filtration for microalgae *C. proboscideum* to produce a slurry with a total suspended solids of 27 wt% (Mohn 1980). Furthermore, two recent studies indicate that a concentration factor of 75–150 was obtained for to produce a cake of >150 g/L solids (Bhave et al. 2012; Zhang et al. 2010). A reduction of 99 % in volume and 90–99 % removal of water were achieved in dewatering (Bhave et al. 2012). The permeate was free of solids. However, for microalgae with small sizes, membrane filtration may be a challenge, due to biofouling of microalgae on membrane surface. At present, large-scale application of membrane technology for producing algal biomass is not common, but small aquaculture farms do frequently use membrane technology for recovering algal cells for feeding shellfish larvae (Borowitzka 1997). With the progress of membrane technology, it is anticipated that membrane filtration will provide a stable, reliable, efficient, and cost-effective dewatering option for large-scale processing of microalgal biomass for the production of biofuel in the near future (Bhave et al. 2012).

In biodiesel production from microalgae, in addition to microalgae harvest and dewatering from diluted culture media, product recovery, such as triacylglycerols (TAG), from wet microalgae is another key aspect, because of energy saving gained from avoiding biomass drying (Giorno et al. 2013). The study of a single unit membrane filtration for simultaneous microalgae (*Nannochloropsis*) harvesting and TAG recovery showed that both regenerated cellulose (RC) membranes with nominal molecular weight cutoff of 100 and 30 kDa allowed to recover permeate with high content of TGA, but the 30 kDa RC membrane gave a higher purity of TGA with less other coproducts (Giorno et al. 2013). A stable of membrane filtration flux of 20–22 L/m².h was observed for both RC membranes. It appears that the combination of a membrane filtration process with an ultrasonic-assisted

cell breakage is a promising technology for oil recovery from wet microalgae cells.

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Membrane Wettability

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The concept of wettability (S) is referred to the ability of a liquid to wet a surface (Hsu et al. 2011). The degree of wettability, also known as a wetting or spreading, is controlled by interfacial forces established between a liquid (L), solid (S), and vapor (V) phase at the minimum equilibrium distance. These interaction types are usually expressed as surface tensions (γ) and can be correlated to the wettability coefficient by a mathematical equation:

$$S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \quad (1)$$

The surface tension, expressed as a force per unit length [N/m] or energy per unit surface area [J/m²], is a direct measurement of the cohesive energy required for minimizing the free surface area at the interface, where the number of similar species is more restricted than bulk and attractive forces are unequal and unbalanced in all directions (Fig. 1).

This parameter and related polar and nonpolar components can be estimated by a set of mathematical equations (Good and Van Oss 1992):

$$\gamma_s^{LW} = \frac{\gamma_l^{LW} \cdot (1 + \cos \Theta)^2}{4} \quad (2)$$

$$\gamma_l \cdot (1 + \cos \Theta) = 2 \cdot \left(\sqrt{\gamma_s^{LW} \cdot \gamma_l^{LW}} + \sqrt{\gamma_s^+ \cdot \gamma_l^-} + \sqrt{\gamma_s^- \cdot \gamma_l^+} \right) \quad (3)$$

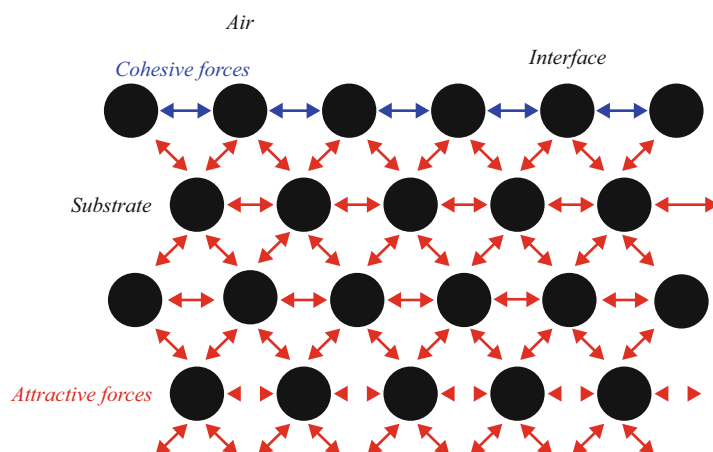
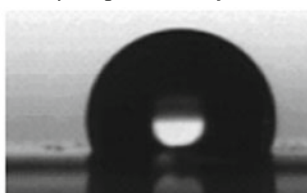
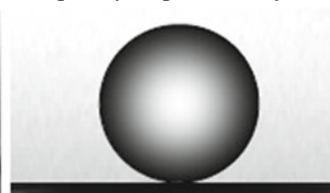
$$\gamma_s^{AB} = 2 \cdot \sqrt{\gamma_s^+ \gamma_s^-} \quad (4)$$

where the Lifshitz–van der Waals forces γ^{LW} [mJ/m²], polar γ^{AB} [mJ/m²], acid (electron acceptor) γ^+ [mJ/m²], and base (electron donor) γ^- [mJ/m²] are the components of the surface free energy γ [mJ/m²] and can be calculated from mean values of the apparent contact angle (θ_a), expressed in a somewhat simplified form by the Young's equation:

$$\cos(\theta_a) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (5)$$

It is a convention to consider $\theta = 90^\circ$ as a boundary value between hydrophilicity and hydrophobicity. Values less than 90° indicate hydrophilic membrane surfaces with a positive liquid spreading, whereas angle values higher than 90° are measured on hydrophobic membrane surfaces with negative spreading values (Fig. 2). Rolling water droplets can be observed on superhydrophobic surfaces with $\theta > 150^\circ$ and $S < < 0$.

In all cases, the apparent contact angle can be regarded as the result of combined morphological (i.e., tailed and loopy polymer segments, grooves, and pores) and chemical (i.e., functional binding

Membrane Wettability,**Fig. 1** Representative scheme of cohesive forces at an interface**a** $S > 0$ $\theta < 90^\circ$
Hydrophilic surface**b** $S < 0$ $\theta < 90^\circ$
Hydrophobic surface**c** $S \ll 0$ $\theta > 150^\circ$
Super-hydrophobic surface**Membrane Wettability, Fig. 2** Water droplets on wettable (a), non-wettable (b), and super-hydrophobic surfaces

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or nonbinding sites) elements. Both two contributions can go to the same or opposite direction, depending on the nature of the chemical and physical forces established at the interface. Normally, large membrane surface affinity toward a liquid produces extensive spreading, while higher surface roughness minimizes it. The roughness factor or rugosity (R) is associated with an irregularity of the membrane surface and can reduce the adhesion between liquid and substrate, causing an increase in the apparent contact angle (Thomas 1999). In this respect, Wenzel and Cassie–Baxter equations describe the wettability better than Young’s equation, which is considered valid for ideal surfaces only (Fig. 3).

In the Wenzel model, the surface grooves are completely filled by the liquid and the contact angle is determined by

$$\cos(\theta_w) = R \left[\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right] \quad (6)$$

Combining this equation with the Young’s one, a simplified relation can be achieved:

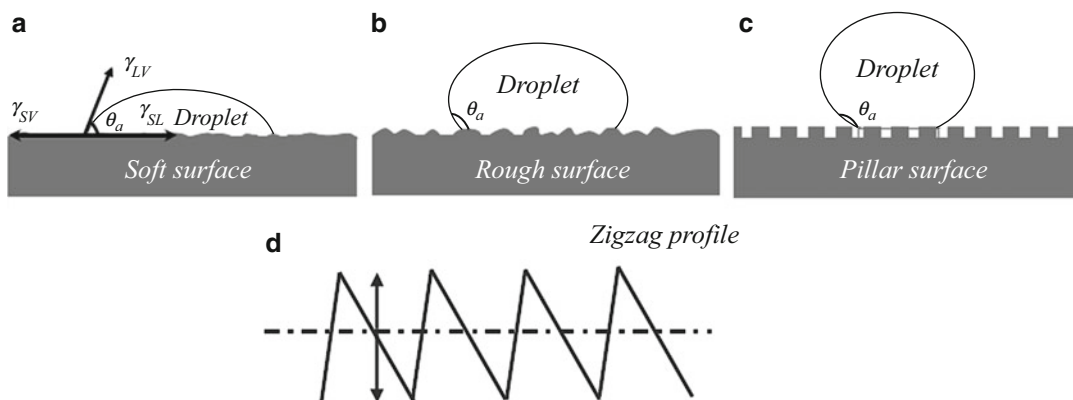
$$\cos(\theta_w) = R \cdot \cos(\theta_a) \quad (7)$$

Instead, in the Cassie–Baxter model, grooves as well as pores are filled by air, which reduces the adhesion line between liquid and substrate, resulting in higher contact angle values:

$$\cos(\theta_{CB}) = f_s \cdot \cos(\theta_a) + f_v \cdot \cos(\theta_v) \quad (8)$$

where θ_a is the angle measured on the flat surface, whereas f_s and f_v are the fractions of the solid and vapor on the surface, respectively.

Some authors have proposed a “zigzag” geometric model that corrects for roughness factor for contact angle measurements, thereby making possible an evaluation of the surface chemistry effects (Taniguchi and Belfort 2002).



Membrane Wettability, Fig. 3 Effects of the roughness factor on the contact line between droplet and surface: (a) a flat surface described by Young's equation, (b) a rough

surface described by Wenzel equation, (c) a pillar surface described by Cassie–Baxter equation, and (d) zigzag profile section responsible for increased surface roughness

Contact angle measurements are powerful tools able to reveal variations of the supramolecular chemistry owing to adsorption, fouling, affinity, or dry–wet switch taking place on the membrane surfaces during separation processes. In this respect, useful indication can be obtained about the opportunity to put in contact membranes with chemical streams without damages and/or special treatments. Cleaning against dirty or chemical contaminations can be monitored as well as energy cohesive can be determined in order to detect the nature of the interfacial forces that control adhesion processes. Also, swelling along with wetting and dewetting phenomena can be studied under the action of specific triggers. Static and dynamic contact angle modes take the advantage of investigating all these supramolecular changes in real time (Gugliuzza and Drioli 2007; Gugliuzza and Drioli 2004, Gugliuzza et al. 2006, 2007). In static mode, a predetermined volume of liquid is placed on the membrane surface and changes against time can be monitored. In dynamic mode, the liquid is constantly pumped into (advancing mode, θ_{adv}) and out (receding mode, θ_{rec}) a droplet in contact with the membrane. The advancing contact angle gives indirect indication about hydrophobic domains distributed throughout the surface; the receding one reveals the ability of local chemical moieties to rearrange when coming in contact with the liquid phase. The

hysteresis expresses the difference between two plateau values, due to chemical and morphological effects at the liquid–surface interface.

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Membrane-Based Desalination

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Desalination (also known as “desalinization” and “desalting”) refers to the removal of salts and other minerals from water. Main drivers for desalination include rapidly expanding population, industrialization, unequal distribution of water resources across the globe, and enriched living standards. On one hand, demand of freshwater is constantly increasing, while on the other hand, the reservoirs of freshwater are becoming contaminated and their size is shrinking. It has been estimated that over one billion people in the world are deprived of clean water and approximately 2.4 billion people are living in water stressed regions. In order to bridge the gap between demand and supply of the freshwater, brackish water, and seawater, desalination has been adopted globally. On the parallel lines, water reuse has been adopted for irrigation, cooling purpose at power generation plants, and industrial process water. The volume of seawater desalination capacities has been recorded as 80 m³/day during 2013 (Villacorte 2014).

Desalination can be accomplished mainly through thermal, chemical, and membrane-based techniques. Thermal desalination is known since centuries, and techniques such as multistage flash (MSF), multi-effect distillation (MED), and thermal vapor compression (TVC) are still in practice in some energy-rich regions. The Middle East accounts for 50 % of the global desalination capacities. Contrary to this, membrane-based processes (mainly reverse osmosis (RO) and to a certain extent nanofiltration (NF)) have dominated the market with 60 % share. NF as a stand-alone process is not effective to produce portable water from seawater, and its use has been restricted only for mildly brackish water

desalination. RO has emerged as a leading technology both for seawater and brackish water desalination, despite the difference in characteristics of the two water sources. What made the RO desalination applicable for practical uses was the development of appropriate membranes with high permeability and selectivity together with improvement of mechanical strength. The large market share of RO and further predicted increase are due to reduction in energy from thermal to membrane desalination (around a factor of 10) which also decreases the production cost of freshwater. Although the energy source has been changed from thermal to electric energy, the main cost breakdown for seawater RO desalination is still the cost of energy. Membrane replacement only accounts for around 10 %.

Despite its widespread application in desalination sector, RO still suffers certain limitations including rigorous feed pretreatment, limited recovery factor, fouling, relatively high energy cost, and brine disposal issue (Greenlee et al. 2009). The basic objective of pretreatment applied is to reduce the fouling tendency of the membrane. Surface water used in seawater desalination has more fouling triggering contaminants and therefore requires more rigorous pretreatment than groundwater. Membrane degradation caused by disinfection treatment applied and biofouling have been considered as big challenges for RO process. New membrane materials with improved chlorine attack resistance are being developed to address the former issue. Seawater desalination capacities located in the coastal areas pose a continuous threat to local environment and marine life due to high salinity level and temperature of the discharged brine.

In order to address the problems associated with reverse osmosis desalination, better energy recovery devices, better membranes, and very large-scale plants with twice the capacities of today's RO desalination plant are being investigated. Moreover, a very interesting approach for improve desalination is the integration of various membrane operations. The combination of innovative and well-established operations for desalination offers highly interesting opportunities. Actual experimental data suggests that, if MD is

operated on the RO retentate, the total amount of desalinated water represents almost 88 % of the feedwater. Additionally, the use of a membrane crystallization allows extracting not only further water but also the minerals contained in the brine streams (e.g., sodium, chlorine, magnesium, sulfate, calcium, potassium, bicarbonate, and eventually also lithium, bromine, etc.). The integration of forward osmosis or reverse electrodialysis for energy production from salinity gradient might be a strategic intensified desalination industrial sector in the future. Integrated approach takes into account energy saving, water rationalization, minimization of resources utilization, and waste production and can contribute significantly to the solution of strategic aspects of industrial productions. Different membrane operations can be coupled in integrated systems for approaching the ambitious objective of “zero liquid discharge” in desalination (Drioli and Criscuoli 2011).

Due to the rapidly growing demand of freshwater, a lot of research activities are being conducted to find new ways to carry on desalination. Emerging processes including electrodeionization, membrane distillation, freeze separation, capacitive deionization, rapid spray evaporation, vacuum distillation, etc. can reshape the desalination system of future. Furthermore, the current desalination techniques will have to cope with new challenges of successful and stable treatment of high salinity streams such as produced water which may contain total dissolved solids many times higher than seawater. The current RO process does not adequately remove some trace elements such as boron. The removal of micropollutant originating from pharmaceutical and personal care products is another challenge to be addressed by the successful desalination technologies of the future.

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Membrane-Based Heat and Moisture Recovery

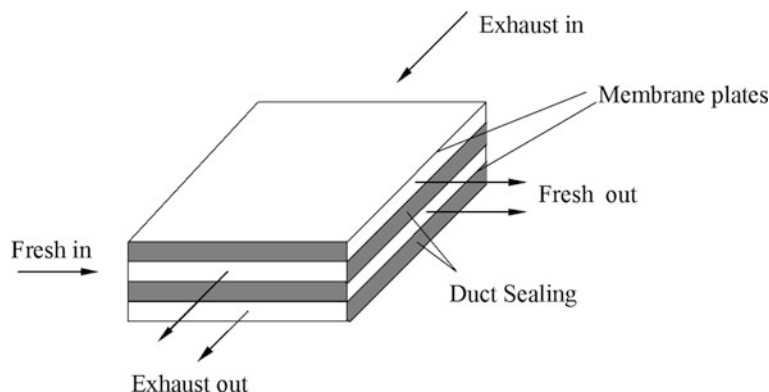
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Membrane-based heat and moisture recovery (also called membrane-based total heat recovery) is the most innovative device used for energy recovery from ventilation air of buildings. Normally the water vapor content of atmospheric air is small, some tens of grams per kilo of air. Nevertheless, due to the very high heat of vaporization, the latent heat content in air conditioning is of the same order of the sensible one. Due to the fact that the fresh air latent load accounts for 20–40 % of the total load for air conditioning and air conditioning accounts for one third of the total energy use in society, to reduce energy use in treating fresh air is a crucial step to the whole society's sustainable development. Total heat exchangers (or the so-called energy recovery ventilators or enthalpy exchangers) could save a large fraction of energy for cooling and dehumidifying the fresh air since cool and dryness would be recovered from the exhaust stream to the fresh air in summer, as shown in Fig. 1. With total heat exchangers, the efficiency of the existing HVAC systems can be improved either. The reason is that normally the fresh air is dehumidified by cooling coil through condensation followed by a reheating process, which is very energy intensive. This part of energy can be saved if total heat exchangers are installed to reduce the dehumidification load. Besides energy conservation, the total

Membrane-Based Heat and Moisture Recovery,

Fig. 1 Schematic of a membrane total heat exchanger (Zhang 2008, 2013)



heat exchangers have the additional benefits of ensuring sufficient fresh air supply, which is crucial for the prevention of epidemic respiratory diseases like SARS and bird flu.

Membrane-based total heat exchangers have many benefits. They have no moving parts and the reliability is quite high. The duct sealing is easy and the crossover problems can be prevented. The difference between a total heat exchanger and a common sensible-only heat exchanger is that water-permeable membrane plates are used instead of metal plates. Currently, there are two types of vapor-permeable materials: paper and hydrophilic polymer membranes. Paper is cheap, but its moisture efficiency is lower than 0.4. Membranes have higher latent effectiveness above 0.65. The shortcomings are that they are expensive than paper. Developed membranes for heat and moisture recovery include dense membranes, composite membranes, and supported liquid membranes. The structures for total heat exchangers include parallel-plate duct, plate-fin duct, and cross-corrugated duct.

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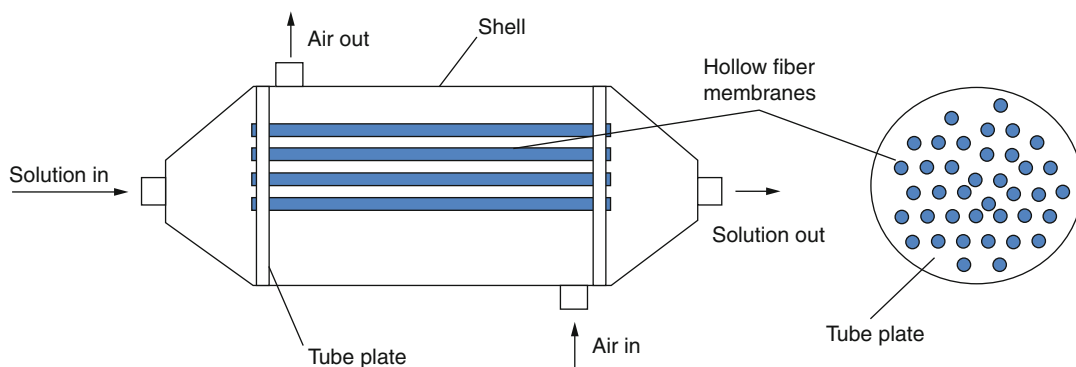
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Membrane-Based Liquid Desiccant Air Dehumidification

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Membrane-based liquid desiccant air dehumidification is the most innovative device used for non-contacting air dehumidification. It is also called membrane contactor for liquid desiccant air dehumidification. Liquid desiccant air dehumidification is one of the most widely used dehumidification technologies for air dehumidification or indoor air humidity control, due to its advantages of high efficiency, no liquid condensate droplets, and its capability of energy storage. Packed beds or packed columns are the common way of processing the air. According to this method, the liquid desiccant is spread down the packings in the column. They provide the large contact areas between the liquid and air stream, on which the liquid is spread. Air stream flows across the packing surfaces. Since the liquid desiccant and the process air are in a direct contact, small liquid desiccant droplets may be carried over by the process air to indoor environment, which is believed to be rather harmful to occupant health, building structure, and furniture. In order to overcome these drawbacks, membrane contactors are



Membrane-Based Liquid Desiccant Air Dehumidification, Fig. 1 Schematic of a membrane contactor for liquid desiccant air dehumidification (Zhang 2008, 2013)

used to replace packed columns. Membranes are used to separate the liquid and the air streams, so it is also called non-contacting air dehumidification. The membranes can prevent the liquid desiccant from crossing over to the process air, while selectively permitting the transport of heat and moisture between the liquid stream and the air stream. The developed membranes include hydrophobic porous membranes and hydrophobic-hydrophilic composite membranes. The structures can be parallel plates or hollow fiber membrane bundles. For liquid-to-air heat and mass exchangers, shell-and-tube structures are suitable. When membranes are made into hollow fibers, they can endure large pressures. Numerous fibers are packed in a shell to form a shell-and-tube structure, which makes the packing densities rather high. Liquid always flows inside the fibers, and gas flows across the bundle. The contact area between the liquid and the gas is very high, which is often used to offset the drawback of slow liquid-air transport coefficients. For such structures, air side pressure drops are usually low and acceptable. Due to tube structure, liquid side can endure large pressures, which makes the driving force high. The benefits are that the pressure drops for both sides are within acceptable levels. The inlet solution is cold and thick. Hygroscopic salt solution like LiCl and CaCl₂ can be used. The dew point for dried air can be $-48\text{ }^{\circ}\text{C}$ (Fig. 1).

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Membrane-Cryogenic Hybrid Processes

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Membrane-cryogenic hybrid processes are processes in which membrane technology and condensation equipment are combined to achieve a gas separation. This type of process is particularly efficient, when at least one component is condensable. Water vapor and higher hydrocarbons are typical gases which can easily be removed from permanent gases by condensation separation.

Membrane-cryogenic processes are particularly interesting when the components which are easy to liquefy permeate faster through the membrane. Here only a fraction of the feed gas has to be chilled. Concerning water almost all membrane materials can be applied. When vapors are to be

separated, rubbery membrane materials should be applied, as the vapor components will permeate faster through the membrane.

The separation in a gas permeation module is determined by kinetics, while the condensation separation is governed by thermodynamic equilibrium. Hence, the outlet concentration of the condensable components from the condensation equipment is determined by the vapor-liquid equilibrium only. It is mainly determined by temperature and pressure. Often, the concentrations of the condensable components are low compared to the concentration of the permanent gases, and, thus, the vapor-liquid equilibrium can be considered as independent of concentration.

Two types of membrane-cryogenic processes can be realized when vapor permeates faster through the membrane than permanent gases. In the first process, the membrane unit performs the main separation, but the permanent gases which should be rejected by the membrane also permeate through the membrane. In order to enhance the recovery of the permanent gases, chilling equipment is applied on the permeate side. Hence, the condensable gases will be removed from the permeate gas and the permanent gases will be recycled.

In the second process, the chilling unit and the gas permeation unit are connected in series. The chilling unit performs the bulk separation, and the gas is further polished in the subsequent gas permeation unit. The permeate stream of the gas permeation module is enriched in condensable components, and this stream is recycled to the chilling unit. Hence, the inlet concentration is increased and the quantity of components which are condensed increases.

Examples of Membrane-Cryogenic Hybrid Processes

The separation of propylene and nitrogen is efficiently done applying a hybrid process in which cryogenic separation and membrane modules are combined (Baker et al. 1998). Rubbery membranes are used and propylene

selectively permeates through the membrane. In this process both the propylene and the nitrogen are to be recovered at high purities. The propylene is obtained from condensation equipment in liquid state so that it has a high purity. The nitrogen purity is controlled by a gas permeation module.

Follmann investigated membrane-cryogenic hybrid processes for carbon dioxide capture (Follmann 2010). Here, chilling and gas permeation membranes are combined to separate carbon dioxide and nitrogen in a postcombustion process. However, driving this hybrid process requires more energy than the conventional amine absorption process.

In the purification of steam cracking products, mixtures of mainly hydrogen, carbon monoxide, methane, and ethylene have to be separated. The hydrogen can be separated in a gas permeation unit where the hydrogen selectively permeates through the membrane (Hopkins et al. 1987). The hydrogen-lean retentate stream is polished in a subsequent cryogenic separation.

Air can be used to produce both high-purity argon and nitrogen (Thorogood et al. 1991). A chilling unit supplies two streams. One is enriched in nitrogen and the other is enriched in oxygen and argon. A gas permeation unit is applied to separate oxygen and argon. Here, the argon preferentially permeates through the membrane, and at least two membrane stages are required to obtain high argon purities.

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Membranes for Biosensors

► Biosensor-Based Membrane

Membranes for Blue Energy

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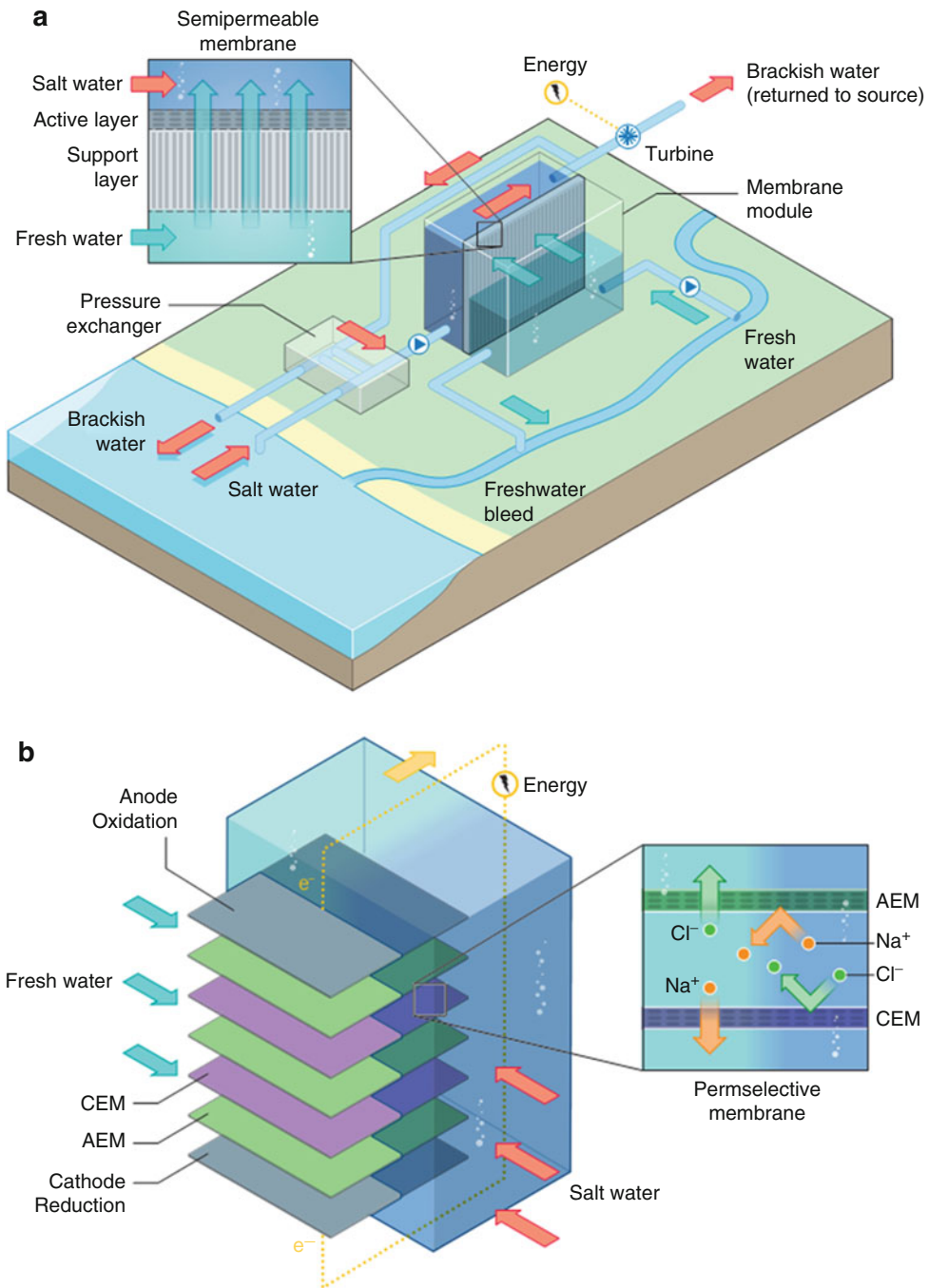
Synonyms

Pressure retarded osmosis (PRO) for energy generation; Reverse electrodialysis (RED)

Blue energy or the salinity-gradient energy refers to the energy extracted from two streams with different salinity levels. By exploiting the salinity gradient between seawater and freshwater, theoretically, 0.8 kW/m^3 can be extracted which is equivalent to a waterfall falling from a height of 280 m (Post 2009). The maximum extractable energy by mixing two streams with different salinity levels ranges from 0.75 to 14.1 KWh/m^3 of low-salinity streams (Logan et al. 2012). The actual quantities are anyhow lower due to inherent irreversible energy dissipation. Among several approaches being investigated, reverse electrodialysis (RED) and pressure retarded osmosis (PRO) are two most commonly used approaches to harness blue energy. PRO is based upon the flow of water through a semipermeable membrane to produce pressurized water that generates

electricity using mechanical turbines. The operational principle of PRO and RED has been explained in Fig. 1a, b, respectively. The semipermeable membrane ideally retains all the ions and allows the flow of water from low concentration to high concentration increasing the pressure of this stream. A part of high-pressure stream is used to run a turbine that generates electricity, and the rest is used to pressurize saltwater by using a pressure exchanger. RED utilizes ion-exchange membranes for ionic transport that directly generates the current. In RED, cation- and anion-exchange membranes are used to transfer the respective ions from high- to low-concentration solution flowing through alternative channels. The electrochemical potential associated with the movement of positive and negative ions is converted into electric current at electrodes.

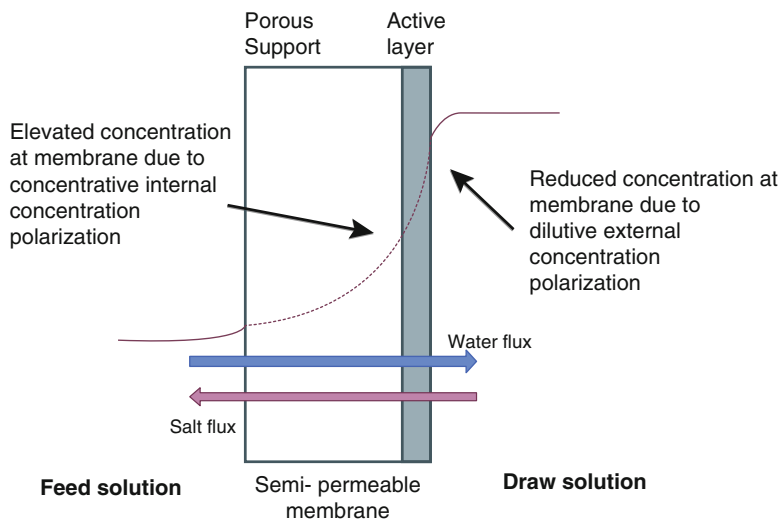
Progress in PRO has been retarded by the lack of suitable membranes that could allow the passage of water at adequate rate. Internal concentration polarization (Fig. 2) occurring in the support of layer of membrane limits remarkably water flux and associated power density. Two mechanisms govern the internal concentration polarization: rejection and accumulation of salt present in the dilute stream and diffusive salt diffusion through the membrane from concentrated to dilute solution. The new generation of cellulose acetate membranes originally developed for forward osmosis is capable to achieve power density as high as 5.1 W/m^2 . The unavailability of robust and fouling-resistant membranes with minimum internal concentration polarization and fouling tendency are the main obstacles for economical commercialization of PRO process. The main focused areas for further improving power density of RED include improvement of membrane material, spacing, and architecture. The main challenge for RED is the high cost of RED membranes that is expected to decrease with increase in global demand (Logan et al. 2012). This trend has already been observed for reverse osmosis membranes where new membrane materials, improved fabrication methods, and large production volumes have reduced the membrane cost substantially over the time.



Membranes for Blue Energy, Fig. 1 Schematic diagram of (a) PRO and (b) RED processes (Logan et al. 2012)

Membranes for Blue

Energy, Fig. 2 Schematic diagram of internal concentration polarization in PRO (Ramon et al. 2011)



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Membranes for CO₂ Capture from Flue Gas

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The control of anthropogenic emissions of greenhouse gases (GHG) is one of the most challenging environmental issues owing to the implications of GHG for global climate change. Among these GHG, CO₂ is the largest contributor in regard of its amount present in the atmosphere contributing to 60 % of global warming effects, although methane and chlorofluorocarbons have much higher greenhouse effect as per mass of gases (Yamasaki 2003). A lot of efforts have been put

on the reduction of CO₂ emission from large CO₂ point sources such as fossil fuel power plants and other industries (e.g., cement, steel and iron production, natural gas sweetening, and biogas upgrading processes). Such plants emit large quantities of CO₂; for example, the fossil fuel power plants are responsible for roughly 40 % of total CO₂ emissions and coal-fired plants being the main contributor. Clearly, coal-fired plants need to be addressed first, especially by retrofitting existing plants.

Different techniques such as chemical absorption (e.g., MEA, MDEA), physical absorption (e.g., Selexol, Rectisol), physical adsorption (e.g., molecular sieves, metal-organic frameworks), cryogenics, and membrane separation could be used for CO₂ capture. Chemical absorption has been widely used in natural gas for over 60 years and separates out relatively high purity CO₂ stream. However, conventional amine absorption technologies are energy intensive and costly, which would result in large incremental costs. National Energy Technology Laboratory (NETL) estimates that amine unit will increase the cost of electricity production by 70 % (Elwell and Grant). Membranes are already an alternative and competitive technology for the selected gas separation processes such as air separation, natural gas sweetening, biogas upgrading, and hydrogen production during the last two or three decades. Membrane technology will become

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Membranes for Natural Gas Sweetening

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Natural gas sweetening (CO₂ removal from natural gas) is mandatory to meet the specifications of natural gas grid. Decision on which technology to use for CO₂ removal from natural gas is mainly dependent on process conditions and the crude natural gas composition. Conventional chemical absorption is well known and has been commercially used for CO₂ removal in various processes and considered as a state-of-the-art technology. However, membrane system shows a great

potential for natural gas sweetening since it possesses many advantages such as small footprint, low capital and operating costs, and environmental friendly and exhibits process flexibility even though it has only 5 % of the market today. Membrane unit cost and CH₄ loss are two crucial parameters used for evaluation of membrane process efficiency, which are mainly dependent on the membrane performance and process design. Some representative suppliers of membrane systems using different materials for CO₂ separation from natural gas are shown in Table 1. Although common polymer membranes for natural gas sweetening are still using cellulose acetate/triacetate and polyimide, the novel, high-performance fixed-site-carrier (FSC) membranes showed a great interest for CO₂/CH₄ separation (Deng et al. 2009a).

High-pressure operation is the main challenge for natural gas processing with membrane system. Membrane plasticization is found to be a well-known phenomenon in most polymer membranes which absorb a high content of CO₂ at high pressure (Donohue et al. 1989; Wind et al. 2004), resulting to a significant decrease of CO₂ permeance as well as selectivity of CO₂/CH₄. The possible strategies to overcome membrane plasticization are cross-linking of membrane material (Wind et al. 2002) and fabrication of mechanical strength-enhanced membranes, e.g., mixed matrix membrane, by adding inorganic fillers into polymer matrix. Adams et al. prepared a 50 % (vol.) zeolite 4A/poly(vinyl acetate) (PVAc) MMM for CO₂ separation from natural gas (Adams et al. 2011). They found that the prepared MMMs can approach Robeson CO₂/CH₄ upper bound, and CO₂ permeability

Membranes for Natural Gas Sweetening, Table 1 Representative commercial membrane systems for CO₂ removal from natural gas

Membrane	Material	Company	Module
Separex TM	Cellulose acetate	UOP	Spiral wound
Cynara [®]	Cellulose acetate	NATCO	Hollow fiber
Prism [®]	Polysulfone	Air Products	Hollow fiber
Cytop	Perfluoropolymers	MTR	–
Medal	Polyimide	Air Liquide	Hollow fiber

remained effectively unchanged with a 63 % increase in selectivity compared to pure PVAc. Their membranes showed a promising application in high-pressure natural gas sweetening. Deng et al. reported that carbon nanotubes (CNTs) reinforced PVAm/PVA blend FSC membrane and presented a good CO₂/CH₄ separation performance (Deng et al. 2009b; He et al. 2014). It shows a much strong mechanical strength which could have possibility to maintain a good separation performance even at high pressure.

Process design for CO₂ removal by membrane system from natural gas depends on the membrane permeability and selectivity, CO₂ concentration in feed stream, specific separation requirement, as well as the location of the plant. Peters et al. conducted process design, simulation, and optimization for CO₂ removal from natural gas using HYSYS integrated with an in-house membrane program (ChemBrane) (Peters et al. 2011). They reported that a two-stage membrane system with a CO₂ permeance 0.3 m³ (STP)/(m² h bar) and a CO₂/CH₄ selectivity 40 is comparable to that of amine process. Although the purity of sweet gas is a little low, it can still achieve the sales gas standards (<2 % CO₂ in natural gas). A combination of hybrid processes comprising a membrane system for bulk removal of CO₂ from crude natural gas feed with an amine unit for final purification to reach the pipeline specification (<2 % CO₂) could be the optimal process for natural gas sweetening. Future direction of natural gas sweetening using membrane systems will focus on the development of high-performance membranes with an active layer on the order of 0.1 μm to compete with the other separation methods. In addition, membranes should also have to be resistant to warm and high-pressure operating conditions and mechanically strong. Membrane plasticization and long-term compaction at high pressure should be further investigated. Moreover, how to predict the long-term performance in commercial application based on the short-term lab-scale tests could be a continuing challenge of membrane system for high-pressure natural gas sweetening.

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Membranes for Seawater Desalination

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Membranes for seawater desalination include several different membrane types based on the diverse technologies used to produce drinkable water from seawater.

Conventional seawater desalination technologies include multistage flash, multi-effect distillation, and vapor compression (collectively known as thermal desalination) and ion exchange. Membrane-based seawater desalination processes include reverse osmosis (RO) where the saline feed is forced through a semipermeable membrane under an external pressure gradient, forward

osmosis (FO) where water permeates through a semipermeable membrane due to a concentration gradient, and electrodialysis where ions permeate through anionic and cationic semipermeable membranes under an external electric field.

Currently, reverse osmosis (RO) plants account for about 70 % of installed plants worldwide, with thermal desalination totaling around 30 % and electrodialysis and ion exchange less than 5 %. Total desalination installed capacity amounts to about 10^8 m³/day, equivalent to about 1 % of the water supply worldwide. Economic analyses have shown that RO plants are competitive compared to thermal installations (Abou Rayan and Khaled 2003), with higher rejection of most solutes, except boron (Cotruvo et al. 2010). This advantage has been further increased in more recent plants with the installation of energy recovery devices and more efficient pumps (Fritzmman et al. 2007).

Reverse osmosis membrane technology has significantly evolved from the first products in the 1950s in terms of materials, form, and modules (Lee et al. 2011). Today, the RO membrane market is dominated by thin-film composite (TFC) membranes consisting of a support layer with large porosity, a microporous interlayer, and a thin selective layer on the upper surface facing the saline feed. This complex structure ensures not only robustness but also ease of processability. Furthermore, it has enabled the use of interfacial polymerization methods to reduce the thickness of the selective layer to minimize transport resistance. The material of the selective barrier layer is generally made of aromatic polyamides, with significant research and commercial investments in finding other suitable polymer compositions. Surface modification of the selective layer is extensively employed to increase chemical resistance and reduce fouling.

Most commercial RO membranes are sold in the spiral wound module configuration, which offers high specific membrane surface area, ease of scale-up, and interchangeability, and can be easily produced from flat sheet TFC membrane (Pearce 2007). Larger modules can also reduce operating and capital costs (Ng et al. 2008), with 16- and 18-in. modules now being offered on the market.

RO membranes require extensive pretreatment steps to remove solids, organic foulants, and, in some cases, chlorine. RO membranes operate at pressures varying from 40 to 70 bar to overcome the osmotic pressure of the saline feed and resistance due to concentration polarization buildup over time. Due to the high pressures applied, RO membranes suffer from compaction as well as significant fouling buildup over time. These factors all contribute to the high energy cost of operating RO plants, despite significant innovation in the last 50 years which has brought RO operations close to the thermodynamic limit (Elimelech and Phillip 2011).

Forward osmosis as a desalination method was first proposed in the 1970s, but the first industrial FO plant has opened only in 2012 in Oman. FO uses a draw solution that has a higher osmotic pressure than seawater to extract water from the saline feed into the draw solution through a semipermeable membrane. Intense research and development is now being focused on novel membranes and draw solutions. Membranes for FO differ from those for RO mainly due to effects of concentration polarization and the need to prevent reverse draw solute permeation. Cellulose acetate membranes, originally developed for RO, have made a comeback for FO uses, particularly due to their hydrophilic surface and good chemical stability (Alsvik and Hägg 2013).

A combination of the two techniques has been recently proposed (Klaysom et al. 2013), though its economic viability and social acceptance are uncertain (Elimelech and Phillip 2011). In this FO-RO hybrid system, wastewater is used as feed in a first FO unit with seawater used as draw solution. The latter is, therefore, diluted before entering the RO stage. The RO concentrate is then fed to a second FO unit as draw solution and, as a consequence, diluted before discharge. To close the cycle, the wastewater feed from the first FO unit is concentrated, thereby reducing its discharge volume as well.

In electrodialysis (ED) an external electric field is used to separate dissolved ions in the saline feed, riving them to oppositely charged ions through ion selective membranes. ED systems consist of a series of cation and anion exchange

membranes separated by spacers through which the concentrate streams and the demineralized water separately flow out of the membrane module. Fouling, which occurs at the electrodes due to the accumulation of ions, can be removed by periodical reversal of the electrodes' polarity.

The charge-based separation mechanism is effective at removing not just salt ions but also nitrates and other charged species (Voutchkov 2013). On the other hand, removal of charge neutral contaminants, such as nutrients or organic substances, is less effective than RO systems. ED is economically competitive compared to RO when TDS of the water source is less than 3,000 mg/L, so far mainly limiting its use to brackish water desalination.

ED membranes tend to be thicker than RO ones and prepared mixing an ion exchange resin with a polymer binder. Requirements for the selection of the resin and binders are low electrical resistance, resistance to osmotic swelling, and long life expectancy (Murray 1995). The latter aspect is crucial as most commercial ED membranes are sold as sealed filter cartridges.

Recent developments and future directions: Alongside continuous optimization of polymeric membranes, there is intense research in novel membrane materials or membrane designs. A promising area of research is the incorporation of carbon nanotubes in thin-film composite membranes to enhance permeability with no compromise on salt rejection (Mattia et al. 2014). In fact, in these RO CNT-TFC membranes, the selectivity is still determined by the selective layer of the TFC, whereas the CNTs, embedded in it, provide a high flux conduit for permeated water molecules. Other nanotube materials, such as boron nitride and silicon carbide, have shown promise in molecular dynamic simulations.

Another emerging class of materials for RO-based desalination is represented by graphene at its derivative, graphene oxide. Initial reports on desalination using graphene oxide membranes show high permeability and salt rejection (Nair et al. 2012), while molecular dynamic simulations have investigated the possibility of high flux/high rejection through nanometer scale defects in a graphene layer (Cohen-Tanugi and Grossman 2012).

In either case it should be noted that the increase in permeability promised by these novel membranes does not automatically translate in a decrease in the energy cost of RO desalination. The latter, in fact, is related to the pressure gradient across the membrane that, as discussed, is already close to the thermodynamic limit. Higher permeability membranes, though, could reduce the footprint of RO plants and decrease the amount of chemicals for membrane cleaning accordingly (Elimelech and Phillip 2011).

Other potential RO membrane materials, at an earlier developmental stage, include aquaporins and polymer dendritic structures (Lee et al. 2011).

Cross-References

- ▶ [Carbon Nanotube Membranes \(CNT Membranes\)](#)
- ▶ [Fouling](#)
- ▶ [Multilayered Thin Film Composite Membranes](#)

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Membranes for Solvent Dewatering

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Membranes are selective barriers which separate binary mixtures by selectively allowing one component to pass through it while restricting the other under the influence of a different driving force. Solvent dewatering refers to dehydration of organic liquids to achieve purity level of >99.9 %. Generally chemical feedstocks, solvents, and products of chemical reactions in the liquid phase are very often a complex mixture of organic components and water. Some of these mixtures are difficult to separate since distillation requires entrainers which are hazardous to the environment (van Veen et al. 2001). Isopropanol-water system is one such example which forms an azeotrope at 12.5 wt.% water. Isopropanol has wide and varied applications and therefore solvent dewatering is required. A membrane process such as pervaporation is useful in breaking the azeotrope or dewatering the isopropanol to desired concentration. Another is that it breaks down the azeotrope by the

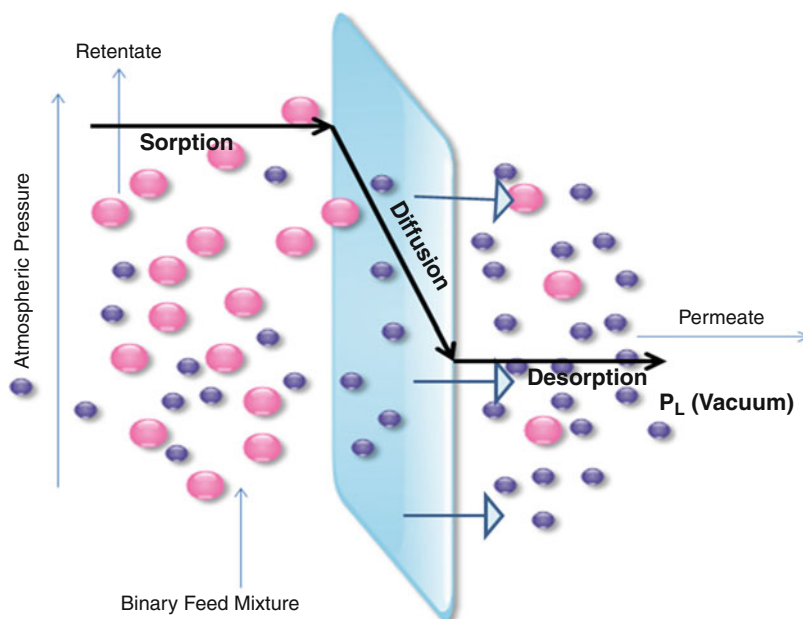
membrane process followed by distillation to attain final purity. A hybrid process of distillation + pervaporation renders dewatering economical. Two types of membrane processes, pervaporation (PV) and membrane distillation (MD), are used in solvent dewatering. Pervaporation allows separation of close-boiling or azeotropic ethanol-water, dioxane-water, acetic acid-water, etc.

Pervaporation (PV) and vapor permeation (VP): PV process finds extensive application in separation of close boiling liquid mixtures, azeotropes, thermally sensitive aromas/flavors and hazardous compounds besides selective removal of species that are present in trace concentrations. Hydrophilic membranes such as poly(vinyl alcohol) (PVA), poly(acrylonitrile) (PAN), poly(acrylic acid) (PAA), sodium alginate, chitosan, poly(ether imide) (PEI), zeolite, and silica membranes coated on tubular ceramic supports have proved to be suitable for solvent dewatering.

PV is generally the combination of two terms: permeation and evaporation. In the permeation step, water solubilizes and diffuses through the membrane, whereas in evaporation step water gets converted into vapor phase due to pressure drop. Figure 1 displays the mechanism of pervaporation process. On the feed side, the organic solvent-water liquid mixture is in contact with the upper surface of the hydrophilic membrane. Water gets sorbed onto the surface of the hydrophilic membrane, then diffuses through the membrane thickness, and finally desorbs in the form of vapor under vacuum at the downstream permeate side of the barrier, leaving behind the dehydrated solvent as the retentate. VP is a process which is very similar through PV except for the fact that the feed in VP is saturated vapor rather than a liquid as in case of PV. VP is also known as evapomeation and is useful when distillation membrane needs to be combined with membrane process. For example, in case of alcohol-water separation, the azeotropic mixture can be separated by directing the vapors from a simple distillation column through the VP unit which enriches the alcohol concentration and thereby provides the advantage of easy separation of the alcohol-water azeotrope. Thus, in VP the flux would be much higher than PV due to the greater

Membranes for Solvent Dewatering,

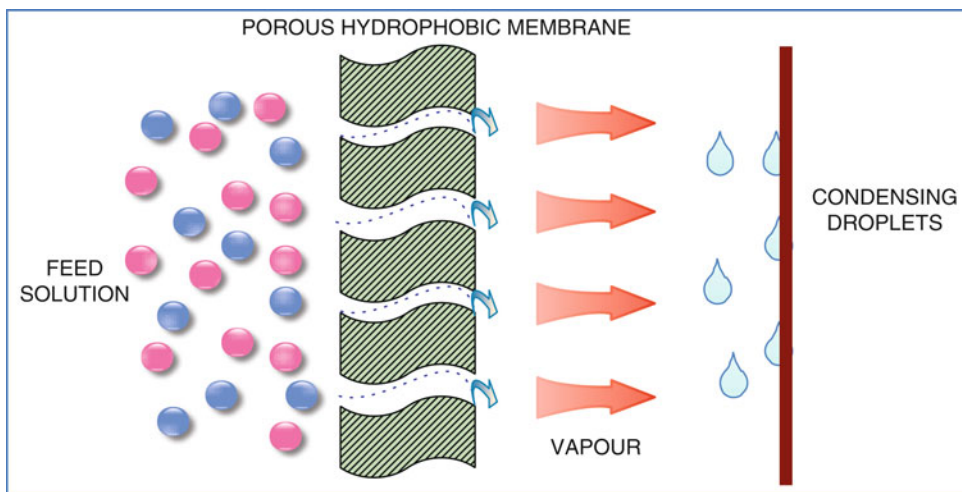
Fig. 1 Principle of pervaporation



enthalpy of the feed, and moreover extra unit operation such as condensation of the distillate or preheating of PV feed can be avoided resulting in lower operating cost. In PV the feed becomes colder with time since the enthalpies for evaporation of permeate are supplied by feed itself which means that the feed needs to be preheated.

Membrane distillation (MD): MD also works on the same principle as PV, but the membrane is of hydrophobic and microporous nature. In MD process water diffusion occurs in the form of a non-isothermal transport of water. In this process the membrane has the property to prevent the liquid from passing through the pores until the pressure of the feed exceeds the critical pressure of the porous barrier (Sina et al. 2009). Due to the difference in temperature, vapor pressure gradient is created on both sides of the membrane pores. At the high temperature side of the membrane, evaporation occurs during which vapor is formed that passes through the pores of the hydrophobic membrane, whereas condensation takes place at the low temperature side of the membrane which means water flows from high temperature side to low temperature side. In MD the necessary condition is that liquid water does not pass through the pores of the membrane and only vapor

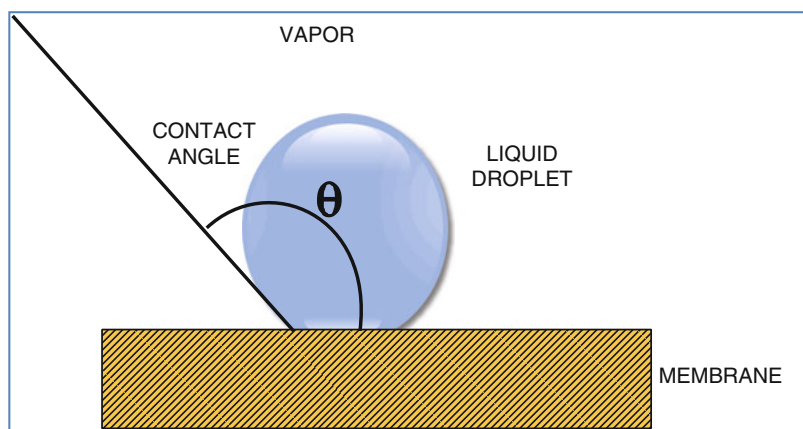
permeates through the pores. During this process the membrane behaves as a physical support for the liquid-vapor interfaces. The nature of hydrophobic microporous membranes is such that it allows the water vapor to penetrate, but due to the surface tension property, it does not allow liquid water to pass through. The driving force for water transport in this kind of process is a gradient in water chemical potential created by a vapor pressure difference. So in this process, diffusion plays an important role, whereas the role of sorption is negligible. MD is useful for different applications such as desalination of water; concentration of liquid foods, sugar solutions, and beverages; and recovery of fermentation products, mineral acids, and aroma compounds including flavors and fragrances, besides treatment of oily feeds. In this process a hot aqueous feed solution is brought into contact with the membrane which prevents penetration of water into the pores due to its hydrophobic nature, resulting in a vapor-liquid interface at each pore entrance. Figure 2 illustrates how the vapor-liquid interfaces are supported at the pore openings. The value of the contact angle θ of a liquid droplet on an ideal smooth homogeneous surface is described by Young's equation (Madhumala et al. 2014):



Membranes for Solvent Dewatering, Fig. 2 Principle of membrane distillation

Membranes for Solvent Dewatering,

Fig. 3 Schematic of a liquid droplet on a solid surface



$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

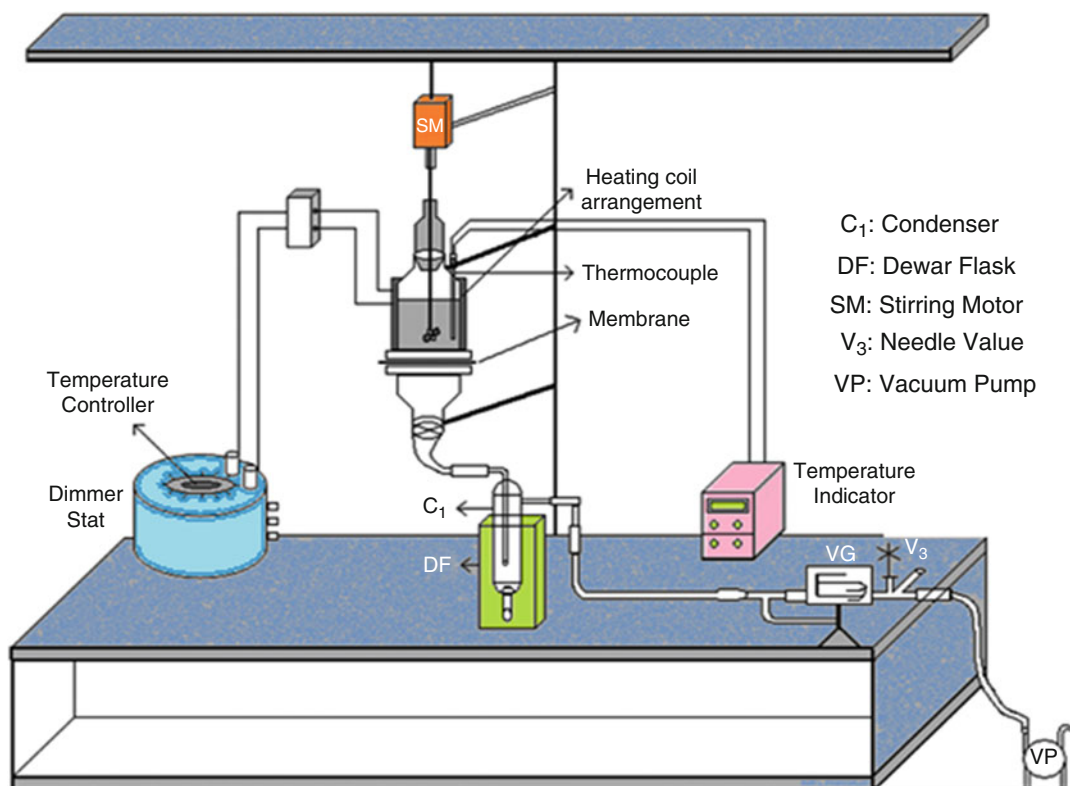
where θ is the contact angle between the liquid and membrane and γ_{lv} , γ_{sv} , and γ_{sl} represent liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively.

A droplet of water on a hydrophobic surface of a polymer film made of say polystyrene (PS), polypropylene (PP), or polytetrafluoroethylene (PTFE) will provide a contact angle which is larger than 90° . If surface active agents or organic materials are dissolved in water, the surface tension of the liquid will decrease. As a result, the contact angle θ will decrease, and if it becomes smaller than 90° , the liquid will wet the solid

surface. A schematic description of contact angle between air, liquid droplet, and solid surface is shown in Fig. 3.

• Experimental setup for PV and MD unit operations

A schematic of PV and MD experimental unit is depicted in Fig. 4. The PV cell consists of two bell-shaped B-24 size glass column reducers/couplers clamped together with externally padded flanges by means of tie rods to give a vacuum-tight arrangement. The top half is used as a feed chamber and the bottom one as a permeate chamber. The membrane is supported by a stainless steel porous plate



Membranes for Solvent Dewatering, Fig. 4 Experimental unit for pervaporation/membrane distillation operations

which is embedded with a mesh of the same material to provide a smooth uniform surface. Teflon gaskets are fixed by means of high vacuum silicone grease on either side of the membrane, and the sandwich is placed between the two glass column couplers and secured tightly.

After fixing the membrane, the cell needs to be installed in the manifold and connected to the permeate line by means of a B-24 glass cone which is fixed to a high vacuum glass valve on one side followed by a glass condenser trap consisting of a small detachable collector. The trap is placed in a Dewar flask containing liquid nitrogen for condensing the permeate vapors. A rotary vacuum pump is used to maintain the permeate side pressure which is measured with an Edwards Mcleod gauge tilting type of scale in the range of 0.01–10 mmHg. High vacuum rubber tubing is used to connect the various

accessories to the experimental manifold. Glass - cone-socket joints are fixed with high vacuum grease. The membrane is soaked in the feed solution overnight to attain equilibrium. During experiments, the upstream side is maintained at atmospheric pressure, and the downstream side vacuum is controlled by adjusting a vent valve for air inlet. The following types of membranes are used for dehydration of organic liquids.

- *Dehydration using polymeric membranes*

Polymeric membranes are widely used in solvent dehydration. The nature of material and chemical structure of the membrane and its substrate determine the performance of the membrane. Mass transfer through such polymeric membranes can be explained on the basis of preferential sorption which is a consequence of inter- and intramolecular structure and diffusion which depends on molecular

Membranes for Solvent Dewatering, Table 1 Literature review on solvent dewatering processes

S. No	Process	Binary mixture	Membrane	Selectivity	Flux (Kg m ⁻² h ⁻¹)	Temperature	Reference
1.	PV	Ethanol/H ₂ O	Polyamide-6	2	1.15	80	Kujawski (2000)
2.	PV	Dioxane/H ₂ O	Polyamide-6	45	0.04	35	Kujawski (2000)
3.	PV	Acetic acid/H ₂ O	Polyamide-6-PAA	82	0.005	15	Huang et al. (1987)
4.	PV	IPA/H ₂ O	PESS Li ⁺	40	0.087	25	Kujawski et al. (1988)
5.	PV	IPA/H ₂ O	PESS k ⁺	60	0.026	25	Kujawski et al. (1988)
6.	PV	IPA/H ₂ O	Chitosan	5134	0.087	30	Devi et al. (2005)
7.	PV	MEK/H ₂ O	PEBA	100	0.12	40	Ravi et al. (2011)
8.	PV	DMF/H ₂ O	Silica membranes	102	1007	100	Van Veen et al. (2001)
9.	PV	n-butanol/H ₂ O	Commercial silica membrane	150	3.53	70	Panagiotis et al. (2014)
10.	PV	THF /H ₂ O	Chitosan/PVP blend	500	0.11	35	Devi et al. (2006)
11.	PV	Ethylene Glycol/H ₂ O	Cross-linked Chitosan	234.26	0.378	32	Rao et al. (2007)
12.	PV	2-butanol/H ₂ O	PVA and nylon 66	26.5	3.07	-	Sridhar et.al (2006)
13.	PV	Ethanol/H ₂ O	NaAlg	≈500	0.1	50	Yeom et al. (1998a)
14.	PV	Ethanol/H ₂ O	Na-Alg/PVP	364	0.09	30	Yeom et al. (1998b)
15.	PV	Ethanol/H ₂ O	PSF	600	0.7–0.9	25	Chen et al. (2001)
16.	PV	Ethanol/H ₂ O	Nylon-4/PVA	13.5	0.42	25	Lee et al. (1992)
17.	PV	Ethanol/H ₂ O	Nafion 811 Li ⁺	11.4	1.644	29	Cabasso et al. (1985)
18.	PV	IPA/H ₂ O	Polyaniline/PAA	>10,000	0.3	80	Xu et al. (2003)
19.	PV	Ethanol/H ₂ O	Polypropylene	4.9	0.175	24	Peter et al. (2008)
20.	PV	Ethanol/H ₂ O	PVDF	35	3.1	50	Peter et al. (2008)
21.	PV	Ethanol/H ₂ O	PAN	281	0.007	50	Okumus et al. (2003)
22.	PV	Ethanol/H ₂ O	Zeolite NaA	5100	3.35	95	Kujawski (2000)
23.	PV	Acetic acid/H ₂ O	Zeolite	150	2.5	75	Kujawski (2000)
24.	PV	Isopropanol/H ₂ O	Zeolite	250	4.0	100	Kujawski (2000)
25.	PV	Ethanol/H ₂ O	Cellulose membrane	125–287	0.1	70	Vinita et al. (2002)

(continued)

Membranes for Solvent Dewatering, Table 1 (continued)

S. No	Process	Binary mixture	Membrane	Selectivity	Flux (Kg m ⁻² h ⁻¹)	Temperature	Reference
26.	PV	Isopropanol/H ₂ O	TFC TbHF	261	2.65	50	Dan et al. (2014)
27.	MD	Glycerol/H ₂ O	Polystyrene	Infinite	0.56	28	Madhumala et al. (2014)
28.	MD	HCL/H ₂ O	PTFE	Infinite	8.57	25	Madhumala et al. (2014)
29.	MD	Chloroform/H ₂ O	PVDF	6.81	0.03185	25	Mohamed et al. (2001)
30.	VP	DMF/H ₂ O	NaAlg/PVP	60	0.986	40	Ebru et al. (2011)
31.	VP	Ethanol/H ₂ O	Zeolite NaA membranes	>30,000	4.5	105	Kenichi et al. (2001)
32.	VP	Methanol/H ₂ O	Zeolite NaA membranes	5700	3.5	105	Kenichi et al. (2001)

PVA polyvinyl alcohol, *PVDF* polyvinylidene fluoride, *PTFE* polytetrafluoroethylene, *PAN* polyacrylonitrile, *NaAlg* sodium alginate, *PVP* poly(vinylpyrrolidone), *PSF* polysulfone, *PEBA* polyether block amide, *PES* poly(ethylenecarbonate), *TFC TbHF* thin-film composite tri-bore hollow fiber membranes

size. Hydrophilic membranes act as molecular sieves and preferentially sorb water molecules. When the membrane swells, flux increases as the voids between the polymer chains increase, and membrane selectivity decreases as the larger molecules find it easier to pass through to the other side.

- *Dehydration using inorganic membranes*

There are several advantages of inorganic membranes over polymeric membranes such as higher chemical and thermal stability besides greater flux due to nonporous structure. Inorganic membranes are mainly made from ceramic, zeolite, or their compounds. Shah et al. (2000) used a pervaporation system for dewatering of methanol, ethanol, isopropanol, dimethylformamide (DMF), acetone, and ethyl acetate with the help of hydrophilic inorganic zeolite/sodium alginate composite membrane. Membranes made from ceramic materials can be operated at higher temperatures and in the presence of corrosive solvents where polymeric membranes fail. They also exhibit better mechanical stability and they do not undergo plasticization which helps to maintain a more constant performance with varying feed concentration. However the inorganic membranes are susceptible to sudden impact through

pressurization or depressurization, which is one of their drawbacks. They require much less membrane area compared to polymeric membranes due to the ability to operate at which facilitates higher flux. Inorganic materials can also be operated with highly reactive compounds due to their chemically inert nature.

- *Dehydration using mixed matrix membranes*

Combining the advantages of both polymeric and inorganic membranes with minimization of their individual drawbacks, mixed matrix membranes are being extensively prepared and applied for solvent dehydration. These membranes consist of a polymeric membrane wherein an inorganic material is dispersed and trapped into the polymer matrix. By adding the inorganic material, the mechanical properties of the polymer get improved, and the free volume of the membrane gets increased for faster diffusion of feed molecules. The main advantage of pervaporation is to break the azeotrope without involving any third component or entrainer which is used in conventional process such as azeotropic distillation (Sunitha et al. 2013). Some previous studies on solvent dehydration have been enlisted in Table 1.

In an earlier study reported in literature, Madhumala et al. (2014) used PTFE membrane for membrane distillation-based recovery of hydrochloric acid and glycerol. Banat and Shannag (2000) studied application of MD for recovery of acetone, butanol, and ether solvents from dilute solutions.

Cross-References

► Water Sorption and Diffusion

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of appropriate technology of processing depends on capital and operational costs; waste amount and their characteristics; appointed targets of the process, e.g., the values of decontamination factors; and volume reduction coefficients. Membrane processes can successfully supersede many noneffective conventional methods applied in nuclear industry. But in some instances, they can also complement these methods while improving the parameters of effluents and purification economy.

Efficiency of waste processing can be assessed on the basis of the decontamination factor (DF) and volume reduction coefficient (VRC):

$$DF = \frac{A_o}{A_p}$$

$$VRC = \frac{V_o}{V_R}$$

where A_o is the concentration of radioactivity in the waste before treatment; A_p , concentration of radioactivity in the waste after treatment; V_o , initial volume of the waste; and V_R , final volume of the waste.

Pressure-driven membrane processes (► [Nuclear Waste Processing: Pressure-Driven Membrane Processes](#)) are the most often used for radioactive waste treatment. Such processes like reverse osmosis, nanofiltration, ultrafiltration, and microfiltration have found application in nuclear power plants for the treatment of liquid low and intermediate radioactive wastes, as well as for processing of institutional wastes. The thermal process (nuclear waste processing by thermal processes), namely, membrane distillation, was tested for concentration of low and intermediate radioactive wastes from applications of radioisotopes.

The application of liquid membranes (LM) for selective recovery of some specific radionuclides from waste and process streams was studied including different types of arrangements: bulk, emulsion, and supported liquid membranes (nuclear waste processing by supported liquid membranes). The latter uses membrane contactors

Membranes in Antibiotic Production

► [Antibiotic Production by Membrane Operations](#)

Membranes in Nuclear Waste Treatment

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Nuclear fuel cycle and application of radioisotopes in research, medicine, and industry generate various types of liquid waste that needs treatment before discharge to the environment. The choice

to immobilize liquid membrane inside the pores; the other process, which applies the membranes for contacting two phases, is membrane liquid-liquid extraction (solvent extraction). Such a process is advantageous in comparison with conventional extraction carried out in the mixer-settler apparatus, since it uses small volume of extracting agent and avoids phase mixing and formation of emulsion. It was tested for separation of actinides in the back end of the fuel cycle (Pabby et al. 2009).

Electrical potential-driven membrane processes using ion exchange membranes were also found as an application for radioactive waste treatment. They comprise such methods like electroosmosis, electrodialysis, and membrane electrolysis. Electroosmosis was used for dewatering a radioactive sludge after filtration or gravitational sedimentation (International Atomic Energy Agency 1994). With this method, high retention factors with minimal membrane fouling were achieved.

Electrodialysis was studied for removal of radioactive ions from low- and intermediate-level radioactive wastes. Inactive compounds like NaCl, Na₂SO₄, and Ca(NO₃)₂ prevalent in the solution, were used as carriers of radioactive ions, such as ²⁴Na, ⁴²K, ¹³⁷Cs, and ⁹⁰Y, present in the waste in small quantities. The decontamination factors for radioactive ions as high as 105 were achieved in this process. Both polymeric and inorganic ion exchange membranes with a good resistance to radiation were employed. Electrodialysis was considered for separation of molybdenum ions and CO₃²⁻ and HCO₃³⁻ from liquid waste containing uranium in hydrometallurgical uranium ore processing (Lounis and Gavach 1997). It was used in combination with diffusion dialysis for separation of ¹³⁷Cs and ⁹⁰Sr from 3 M nitric acid solutions (Mathur et al. 1998). Another application of electrodialysis in nuclear technologies is salt splitting (e.g., Na₂SO₄ decomposition) in the high saline waste with recovery of acid and base (International Atomic Energy Agency 1994). The process gave 12–25 % solution of sodium sulfate, 20 % NaOH, and 20 % H₂SO₄.

Sodium super ion-conducting ceramic membranes – NaSICON – were applied for separation of sodium from radioactive wastes (Fountain et al. 2008) and Nafion membranes for concentration of ¹³⁷Cs. AFN ion exchange membranes were used for the recovery of boric acid from wastewater (Park and Lee 1995). Ion exchange membranes obtained by radiation grafting of polyacrylic acid on a matrix of polyethylene and Teflon were tested for removal of zirconium from solutions containing uranium (El-Sayed et al. 1999). Novel anion exchange membrane was applied to separate ¹²⁵I and ³⁶Cl ions by electrodialysis (Inoue et al. 2004).

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Membranes in the Chlor-Alkali Industry

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Membranes in chlor-alkali industry (also called membranes in chlor-alkali process) is the use of membranes in the production of chlorine (Cl_2) and alkali, sodium hydroxide (NaOH), or potassium hydroxide (KOH) by electrolysis of a sodium chloride solution. Chlorine and caustic soda are products that are widely used in the industry. They are used in producing detergents, herbicides, pesticides, pharmaceuticals, plastics, and soaps. The single largest usage area for chlorine is in the manufacture of polyvinyl chloride (Euro Chlor 2007), while its largest use in inorganic chemicals is for the manufacture of titanium dioxide. In the polyvinyl chloride molecule, more than half its content by weight is from chlorine. The manufacture of some plastics such as polyurethanes and epoxy resins that do not contain chlorine in their molecule also requires chlorine in their process. The main technologies applied for chlor-alkali production are mercury, diaphragm, and membrane cell electrolysis, mainly using sodium chloride (NaCl) as feed or to a lesser extent using potassium chloride (KCl) for the production of potassium hydroxide (Lakshmanan and Murugesan 2014; Euro Chlor 2011).

Membranes in chlor-alkali industry have been used since the 1970s when the development of ion-exchange membranes enabled a new technology to produce chlorine: the membrane electrolysis process. The first ion-exchange membranes were developed at the beginning of the 1970s by DuPont (Nafion) followed by Asahi Glass (Flemion) which installed the first industrial membrane plant in Japan in 1975 due to the pressure of Japanese environmental regulations. Today, it is the most promising and fast-developing technique for the production of chlor-alkali and it will undoubtedly replace the other two techniques in

time. Since 1987 practically 100 % of the new chlor-alkali plants worldwide apply the membrane process. Global chlor-alkali production capacity in 2008 was 62.8 million tons/year, with the fastest growth recorded in China, making China today's largest producer and consumer of chlor-alkali products (IPPC 2014). With the growth in membrane cell and conversion to membrane technology, as at 2011, mercury process capacity stood at below 10 % of global production capacity and is set to decline further. Japan is the first major chlor-alkali-producing country to switch entirely to membrane cells (O'Brien et al. 2005).

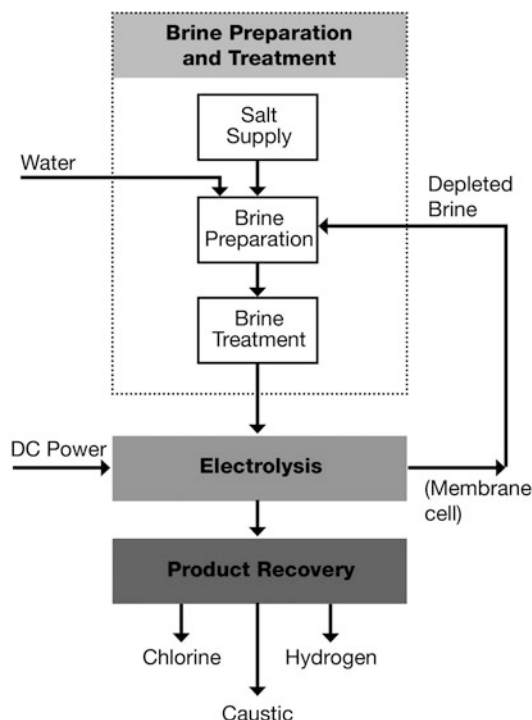
In addition to ion-exchange membranes, the chlor-alkali industry represents a potential field of application for other membrane technologies due to the several and complex brine treatments due to the stringent requirements for brine purity imposed by membrane cells and also during the product's recovery stage. The chlor-alkali process can be divided into three major steps: brine preparation and treatment, electrolysis, and finally product recovery as can be seen in Fig. 1.

Brine Preparation and Treatment

The brine process includes the supply of salt, its dissolution, and purification of the resulting brine to the standards required by the cell technology. The first step is the removal of hardness and heavy metals by precipitation with OH^- and CO_3^{2-} . The precipitates form sludge, removed by settling in a clarifier. The clarifier overflow will have some residual suspended solids which are removed by filtration in two steps (primary and polishing). Then, hardness is reduced to less than 20 ppb by ion exchange, using resins developed specifically for this purpose. The final step in brine preparation is acidification. Two kinds of membrane technology are used in this stage, microfiltration and nanofiltration (O'Brien et al. 2005).

Microfiltration

Microfiltration refers to filtration processes that use porous membranes to separate suspended particles with diameters between 0.1 and 10 μm . This



Membranes in the Chlor-Alkali Industry,
Fig. 1 Major steps in membrane cell chlor-alkali process

technology can be used in brine filtration for removal of precipitates in the primary treatment prior to electrolysis. The ultimate achievement in the chlor-alkali brine process would be to take treated brine from the precipitation reactors and filter it directly in a single step to produce clear filtrate. This would combine the functions of the clarifier, the primary filters, and the polishing filters in a single step.

The type of membranes used in this application is made from poly(tetrafluoroethylene) (PTFE) and has the advantages of controlled pore size, great chemical resistance, and low-energy surfaces (Baker 2000; O'Brien et al. 2005). This kind of polymer makes the membrane extremely inert and thus convenient for processing even harsh streams.

Unfortunately, the particles being filtered often foul the membrane by blocking the membrane pores and/or by forming a cake layer on the membrane surface (Mores et al. 2000). One method of reducing membrane fouling is rapid backpulsing.

A backpulse of low-pressure compressed air (ca. 30 kPa) then forces filtrate back through the element and removes the solids from the membrane surface. This method entails reversal of the permeate flow through the membrane for very short periods (typically less than 1 s) at high frequency (typically once every few seconds). The reverse flow can provide in situ cleaning by removing some of the foulants from the membrane surface or pores (O'Brien et al. 2005).

Nanofiltration (NF)

This process is, along with backpulse filtration, another example of the new possibilities in processing that are due to recent developments in the field of membrane technology. At conditions intermediate between those used in ultrafiltration and reverse osmosis, this technology can selectively reject multivalent ions such as sulfate while passing monovalent ions. The polymer NF membranes systematically reject sulfates up to 98–99 % from concentrated electrolyte solutions. At the same time, the rejection of chloride ions is quite low. This very high sulfate rejection from concentrated electrolyte solutions is useful for a number of practical applications, e.g., the sulfate removal from brines in chlor-alkali electrolysis. The process therefore can remove sulfate and other multivalent anions selectively from alkali chloride brines. The rejection of salts by NF membranes is complicated and depends on both molecular size and Donnan exclusion effects caused by the acid groups attached to the polymer backbone. Charged groups tend to exclude ions of the same charge, particularly multivalent ions while being freely permeable to ions of the opposite charge (Baker 2000). Usually, the sulfate/chloride selectivity in NF is explained by a negative membrane fixed charge.

The membranes used in this application are in spiral-wound modules placed in cylindrical housings. The low-sulfate permeate flows through the membranes into spacer channels fabricated from a supporting mesh and follows the spiraling channels into a central collecting tube. The reject, high in sulfate, leaves the end of the module. Parallel installation of modules allows increased capacity, and series installation increases the recovery of

brine. Several reports on the process indicate that typical membrane cell depleted brine can be concentrated to 80–100 g/L Na_2SO_4 . The chloride concentration may remain the same as in the feed solution or actually decline to a lower level. The process has application regardless of the type of chlor-alkali cell in use, and it also can remove sulfate from chlorate plant liquors (O'Brien et al. 2005).

Electrolysis

In the electrolysis process, a chloride-salt solution is decomposed electrolytically by direct current. There are three basic processes for the electrolytic production of chlorine. These three processes are the diaphragm cell process, the mercury cell process, and the membrane cell process (1970) (ion-exchange membranes). Each process represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced, directly or indirectly, at the cathode (O'Brien et al. 2005).

The Ion-Exchange Membrane

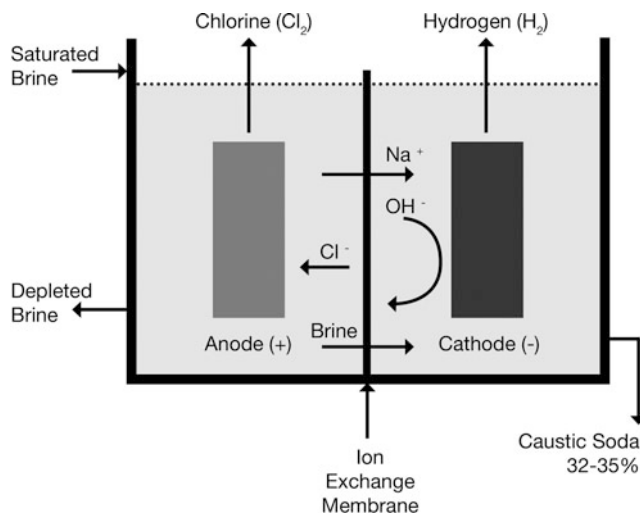
The ion-exchange membrane separates the cathode side from the anode side as shown in Fig. 2.

The membrane currently used in chlor-alkali industry is comprised of two layers to be able to withstand the significantly different conditions on either side of it. The two layers are made of perfluorosulfonic acid and perfluorocarboxylic acid films. Figure 2 shows the membrane cell process. A saturated brine solution that has been previously treated is channeled to the anodic compartment while demineralized water is fed to the cathodic compartment. During the electrolysis, sodium ions and some water permeate through the membrane and enter the cathode compartment. Chlorine gas is formed in the anode. Ion-exchange membranes are classified by their function as a separator; cation-exchange membranes, that contain fixed negatively charged ions, are used in the electrolysis process to prevent the anion transport from the cathode compartment to the anode compartment. The fixed ions of the membrane are in equilibrium with the mobile ions (referred to as counterions) whereas the ions that carry the same charge as the fixed charge (referred to as co-ions) are more or less efficiently excluded from the membrane matrix (Donnan exclusion effect). The most important characteristics of an ion-exchange membrane are high permselectivity for the counterions (exclusion of co-ions), high ionic conductivity, and good mechanical, form, and chemical stability (O'Brien et al. 2005).

M

Membranes in the Chlor-Alkali Industry,

Fig. 2 Membrane cell process in chlor-alkali industry



Product Recovery

Full processing of chlorine gas takes a hot, wet vapor at approximately atmospheric pressure and converts it to a cold, dry liquid under significant positive pressure. The common processing steps therefore are cooling, drying, compression, and liquefaction. Furthermore, electrolytic hydrogen is quite pure and is acceptable for most applications. Normal processing involves cooling, which may also serve to remove entrained caustic, and compression. Hydrogen frequently is cooled by direct contact with brine (O'Brien et al. 2005).

Membranes for Chlorine Separation

In this process the chlorine is purified by liquefaction, this purification step is needed because of impurities in the brine and air leaking into the system during electrolysis. Current technology for the purification of Cl_2 usually involves cooling, drying, compression, and possibly liquefaction, unit operations, which demand heavy and expensive equipment. The separation of gases by thin barriers termed membranes is a dynamic and rapidly growing field. Membranes are being used to separate gases from their mixtures by the differential permeation of the components through them (O'Brien et al. 2005).

The main challenge of this technology is to find a membrane material tough enough to withstand the aggressive chlorine environment at the given process conditions. Additionally the membrane must have an acceptable flux and high selectivity for chlorine compared with the other gaseous components present. Polydimethylsiloxane (PDMS), perfluorinated materials (PTFE and the like), carbon molecular sieve membranes (CMS), and glass membranes have been tested out at laboratory scale and found to be able to withstand the harsh process conditions. Some of these materials showed low permselectivity or low to medium durability, when applied as a gas separation membrane for chlorine separation. However, there are some indications that the membrane challenge may be solved in the future for this separation (Lindbråthen and Hägg 2009).

Electrodialysis in Brine Adaptation for Chlor-Alkali Industry

Brine adaptation for the chlor-alkali industry is a technology strategy available for offsetting the cost by selling the concentrated brine to another industry. From an energy point of view, producing the brine for the chlor-alkali industry starting from a reverse osmosis (RO) concentrate requires less energy to concentrate NaCl than starting from seawater. Moreover, the H_2 obtained could be used in situ for generating electricity, thus, some of this consumption could be self-supplied, which makes this process appropriate for places where energy costs are especially high. Adaptation for the chlor-alkali industry reduces the amount of land required and contributes to reducing capital costs, especially where land is expensive or even not available.

However, divalent cations are also more concentrated in the RO brine and require removal, which involves high costs. This problem has been overcome by producing NaCl and then generating the necessary brine. Tanaka et al. (2003) found that the energy consumption in a salt manufacturing process using electrodialysis (ED) with seawater RO brine was 20 % less than the energy consumption if using seawater. ED is an electro-separation process that uses electrical potential difference as a driving force to move ions through ion-exchange membranes. ED can be used to concentrated brine solutions similar to effluents from the desalination of brackish and industrial water. ED can increase the concentration of a brine solution from 0.2–2 % to 12–20 % with energy consumption in the range of 1–7 kWh/m³.

Further research is necessary in this technological scheme for brine adaptation, especially related to the creation of chlor-alkali plants annexed to desalination facilities. These new plants would give an added value to the generated brines as raw material for the production of Cl_2 , H_2 , and NaOH. Furthermore, chlorine could be used for chlorination of the public water supply. Brine adaptation for the chlor-alkali industry requires processes to concentrate the brine such as ED. It is also necessary to eliminate the divalent cations in brine because they exceed the

specifications for membrane electrolysis. These treatments involve high costs, which can be offset by the products obtained from electrolysis (Morillo et al. 2014).

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Membrane Permselectivity

► Permselectivity

Membranes Used for Bioreactors

► Bioreactor Membrane

Membranes Used for Membrane Emulsification

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In membrane emulsification (ME) method, a microporous membrane is used to disperse one of two immiscible liquids into another liquid. Specific membrane properties are required for the preparation of an ideal emulsion most suited to an intended application (Charcosset 2009; Gijsbertsen-Abrahamse et al. 2004). The most important membrane parameters for emulsification are:

- Pore size
For direct membrane emulsification, the average droplet size (d_d) is mainly determined by the pore size (d_p) by a linear relation:

$$d_d = x d_p$$

where x is typically in range of 2–10. Monodispersed emulsions can be generated if the membrane pore size distribution is sufficiently narrow.

- Pore geometry
Droplets uniformity and productivity are influenced by pore geometry. Round, square, and rectangle pores have been applied in droplet preparation. Noncircular pores have superior performance, in terms of size distribution control and throughput, compared to circular pores. Different phenomena such as interfacial interaction/instability could occur associated with pore geometric factors to favor production of uniform particles at a high throughput.
- Membrane surface porosity and inter-pore distance
Droplet uniformity and productivity are influenced by the membrane surface porosity

Membranes Used for Membrane Emulsification, Table 1 Inorganic membranes used in membrane emulsification

Membrane	Wettability	Pore geometry	Porosity (%)	Pore size (mm)	Membrane form	Producer	Producer country
SPG	Hydrophilic/hydrophobic	Symmetric interconnected cylindrical pores	50–60	0.1–20	Tubular and flat	SPG Technology Ltd	Japan
α -Al ₂ O ₃	Hydrophilic	Asymmetric interconnected cylindrical pores	35	0.1	Tubular	Westfalia separator membraflow	Germany
α -Al ₂ O ₃ /ZrO ₂ coated	Hydrophilic	Asymmetric interconnected cylindrical pores	60	0.02–0.1	Tubular	SCT	France
Silicon nitride	Hydrophilic	Asymmetric cylindrical pores	–	0.2–5	Flat	Aquamarijn™	The Netherlands
Nickel	Hydrophilic/hydrophobic	Symmetric circular or rectangular pores	0.05–25	5–40	Tubular and flat	Micropore Technology Ltd	UK

and distance between pores. Membrane porosity should be low enough to prevent pores to be close to one another and therefore droplets coalescence at the membrane surface before droplet detachment. However, low dispersed phase flux is obtained because of the low fraction of active pores.

- Membrane thickness

The droplet size is indirectly affected by the membrane thickness. At a given transmembrane pressure, the dispersed phase flux increases if the membrane thickness is decreased. Droplets could be generated at membrane pore level faster than emulsifier diffusion rate and larger droplet size could be produced.

- Membrane surface wettability

The membrane surface should be wetted with the continuous phase to obtain droplets of the dispersed phase. The dispersed phase contact angle with the membrane wetted with the continuous phase should be higher than 90°. Hydrophilic membranes are suited to making o/w emulsions and hydrophobic membranes for w/o emulsions. If the membrane is not wetted with the dispersed phase, a monodispersed emulsion will be able to be successfully obtained; however low productivity is achieved.

Two types of membranes can be used in ME:

- Static and fixed membranes in which a moving continuous phase promotes the droplet detachment from the membrane surface
- Moving membranes in which the membrane is rotated or vibrated within the otherwise static continuous phase generating the surface shear

The most commonly used membranes for ME are Shirasu porous glass (SPG) membrane and microsieve membranes. SPG membrane is a symmetric membrane with interconnected and tortuous pores, synthesized from a Japanese volcanic ash (Shirasu). SPG membranes are commercially available by SPG Technology Ltd with pore diameters in the range of 0.1–20 μ , tubular or disk shape, hydrophilic and hydrophobic surface. Microsieve membranes differ from conventional membranes by their well-structured morphology and controlled porosity, which results in dispersed phase flux. Typical microsieve membranes used in ME are silicon nitride microsieve membranes and nickel membranes. Ceramic and polymeric membranes are also used. Membranes used for emulsification and some of their characteristics are summarized in Tables 1 and 2.

Tailor-made microengineered membranes having uniform pore size distribution, pore size in the range

Membranes Used for Membrane Emulsification, Table 2 Polymeric membranes used in membrane emulsification

Membrane	Wettability	Pore geometry	Porosity	Pore size	Membrane form	Producer	Producer country
PTFE	Hydrophobic	Symmetric interconnected cylindrical pores	—	1.8	Hollow fiber	Microdyn module	Germany
			79 %	1 mm	Flat	Advatech Tokio Ltd	Japan
			79 %	0.5–5 mm	Flat	Goretex	Japan
Polyamide	Hydrophilic	Asymmetric interconnected tortuous pores	—	10 and 50 kDa	Hollow fiber	Forschstung Institut Berghof	Germany
Polycarbonate	Hydrophilic	Symmetric parallel pores	5–20 %	0.05–12 mm	Flat	Millipore Inc	USA

from nano- to microscale, asymmetric wettability between the pore wall and the detachment surface, and suitable porosity have to be developed in order to fulfill properties required to produce uniform emulsions with target size and high productivity.

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Mesophilic Organisms

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Mesophiles are microorganisms which grow at moderate temperatures between 20 °C and 45 °C and with an optimum growth temperature in the range of 30–39 °C. They are isolated in both soil and water environments; species are found in the Bacteria, Eukarya, and Archaea kingdom. For

instance, many bacterial species involved in biodegradation (i.e., digestion and decomposition of organic matter) are mesophiles. Similarly, most pathogens that are dangerous to animals and humans are growing at the normal human body temperature (37 °C); some of the most risky mesophiles are *Streptococcus pyogenes*, *Streptococcus pneumoniae*, *Staphylococcus aureus*, *Salmonella* sp., *Proteus vulgaris*, and specific strains of *Escherichia coli*. However, most probiotic organisms (living microorganisms that reach intestine and thus confer beneficial effects to the host) are mesophiles; in particular lactic acid bacteria are largely used in the dairy industries; few strains proved to sustain well-being and prevent gastrointestinal disorders are used in food supplements and nutraceutical preparations. Many food transformations and processing are based on the use of mesophilic microorganisms; in fact brewing (beer production) consists in soaking a starch source, like maize, exploiting specific yeast strains to convert it into ethanol. Wine-making is based on the use of yeast and other bacteria (malolactic metabolism), to achieve ethanol fermentation and flavorings. Cheese and yogurt making are often based on lactic acid bacteria fermentation. However, mesophilic bacteria are also involved in food contamination and degradation. For instance, *Listeria monocytogenes* is responsible for meat, salami, and soft-cheese spoilage. *Escherichia coli* and *Clostridium kluyveri* cause food modification and also may be responsible for gastrointestinal disorders.

Mesophiles may duplicate by cell division through mitosis, or by sexual reproduction with a male or female bacteria. At the optimal temperature, with the pH and salinity, mesophiles can double their population in just 20–30 min. Among mesophiles, *Escherichia coli* is the major bacterial platform for expressing heterologous proteins; it has been used to expand plasmid DNA and to express mammalian proteins and also extremophilic enzymes (extremozymes), permitting to increase enzyme yield. For this reason, growing *E. coli* to high densities has been a milestone since the early 1970s, in order to achieve maximum productivity especially in commercially relevant products. Research strategies were focused on improving the cultivation techniques, manipulating the bacteria's physiology, or both. As a result, batch, fed batch, and in situ product removal fermentation techniques had been developed (Zelić et al. 2004). Among these, membrane bioreactor-based strategies proved to be very efficient together with optimization of media composition, and the application of molecular biology methods canceling to grow *E. coli* to cell densities of up to 190 g/l (dry weight) (Nakano et al. 1997; Shiloach and Fass 2005), by preventing acetate accumulation and increasing recombinant product yield. Membrane bioreactor was also successfully used to improve biomass yield of probiotic strain and lactic acid productivity (Schiraldi et al. 2003).

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Mesoscopic Transport Simulation

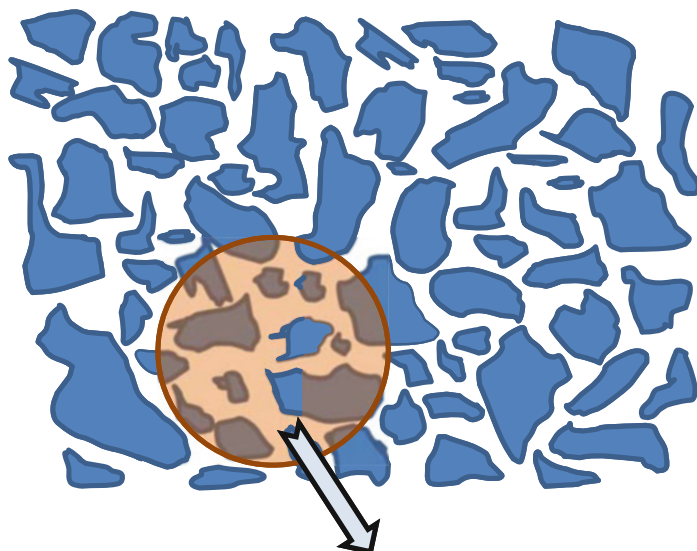
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Mesoscopic transport simulation is a type of conceptual or computational simulation of transport phenomena at the mesoscopic scale. The latter is defined as an intermediate scale between the microscopic scale, which considers molecular configurational details, and macroscopic scale, at which certain types of inhomogeneities or fluctuations have been averaged out. In the area of porous media, mesoscopic simulation of transport phenomena may refer to the pore scale itself, that is, to the scale of a few hundreds of pores or grains or to the scale at which a pore neighborhood is viewed as a thermodynamic point in space. In the former case, the characteristic length of a mesoscopic transport simulator is significantly larger than the atomic dimensions, and, as such, it contains or refers to a large number of molecules of the transported species. As a result, local values of system properties, like density, pressure, temperature, etc., can be defined in a consistent yet statistical manner. In the latter case, a continuum formulation is used to employ spatial averages over length scales much larger than the typical pore or grain scale. The concept of the thermodynamic point or of a representative volume element (RVE) has contributed critically in this direction, sidestepping the need for treating spatial heterogeneities at smaller scales. These are reflected in pore-scale simulations, which are utilized to offer effective values for constitutive parameters that are functions of the local conditions and local structure (Bear 1972). In the context of transport phenomena in membranes, mesoscopic simulations of diffusion, flow, two-phase flow, dispersion, and ionic transport are typical examples of simulations that are performed with reference to finite samples of the membrane material. Once a mesoscopic description of the membrane sample

Mesoscopic Transport Simulation,

Fig. 1 Representative element of porous medium



Representative element of porous medium

is available, transport simulations can lead to the determination of transport coefficients at that scale.

The mesoscopic description of the membrane material may involve a pore model to represent the void space of the membrane, a fiber or grain model to represent the solid phase, or a digitized model of the structure following three-dimensional reconstruction. Different types of numerical tools and simulation techniques have been developed for the solution of problems involving transport phenomena at this scale. Notable examples include the classical numerical solvers for the direct solution of the transport equations complemented by appropriate boundary conditions at the faces of the working domain and at the interface between void and solid or, more generally, between the various phases that comprise the membrane. Typical examples of such equations include the diffusion equation, the heat conduction equation, the Stokes or Navier–Stokes equations for flow problems, the convection–diffusion equation, etc. Another category involves the simulation of the motion of a number of molecule deputies that carry, in an efficient manner, the properties of the actual fluid molecules that are obviously too many to

follow individually. Such methods include the direct simulation Monte Carlo (Bird 1963, 1976, 1994), the dissipative particle dynamics (Hoogerbrugge and Koelman 1992; Moeendarbary et al. 2009), the lattice gas method (Frisch et al. 1986; Wolfram 1986, Rothman and Keller 1988), and the lattice Boltzmann method (Benzi et al. 1992; Chen et al. 1992), which, rather than the fluid molecules themselves, follow the evolution of their probability density function across the lattice. The lattice Boltzmann method is a mesoscopic method that originated from the classical statistical physics and is based on simplified kinetic equations. A rigorous mathematical analysis that starts from the lattice Boltzmann equation has been shown to recover mesoscopic continuity and momentum equations using well-defined features of propagation–collision dynamics. Thanks to the explicit relation with details of the geometry and physics of the problem, complex boundaries and various physicochemical phenomena can be treated. Single- and two-phase flow phenomena with or without phase transition can be studied in the context of membrane separations, including gas separation, filtration, membrane distillation, membrane emulsification, etc. (Fig. 1).

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Metal Removal and Recovery by Supported Liquid Membranes

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Supported liquid membranes are based on the combination between membrane separation techniques and liquid-liquid extraction and also

combining both the extraction and re-extraction processes in a single step. They may be applied for the separation of many chemical species, both organic and inorganic, including metals. In the case of metal separation, they use a three-phase configuration, with a thin layer of organic phase impregnating the pores of a solid membrane (polymeric or ceramic) which separates two aqueous phases of different compositions; one of them is the source phase that contains the metals to be separated and the other one is the receiving solution that normally includes a chemical reagent to facilitate the re-extraction process (Fig. 1).

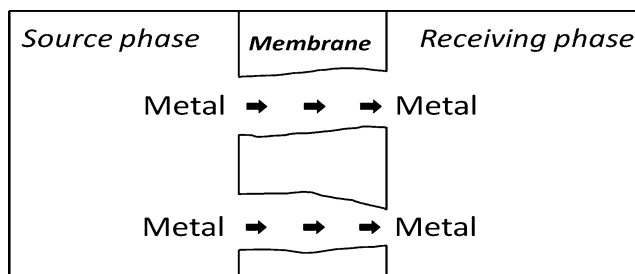
In most cases, the liquid membrane contains an organic selective reagent that facilitates the transport of metals through it acting as a carrier. This organic reagent may be an ionic (both cationic or anionic) or neutral compound, defining a transport mechanism based on ion exchange or solvation, respectively. Besides, different physical configurations of supported liquid membranes may be used, which can be classified in three groups: flat-sheet membranes, hollow fiber membranes, and, in lower extend, spiral wound modules (Dzygiel and Wiczorek 2010).

The use of supported liquid membranes for metal separation has been mainly restricted to laboratory scale. Large-scale operations of supported liquid membranes have been considered a difficult task, basically due to their low stability under long-term operation, which has been associated to the loss of the organic phase filling the pores of the solid membranes. However, the increasing commercialization of hollow fiber modules may contribute to its industrial application.

In the last few years, big attention has been paid to the use of supported liquid membranes as a

Metal Removal and Recovery by Supported Liquid Membranes,

Fig. 1 Schematic representation of a supported liquid membrane used for metal separation



tool for sample preparation in analytical applications. In this sense, liquid phase microextraction systems based on hollow fibers are normally developed, with special interest in miniaturization and optimization of metal enrichment factors.

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Metal-Organic Framework

► ZIF-8 Membrane

Metal-Organic Frameworks (MOFs)

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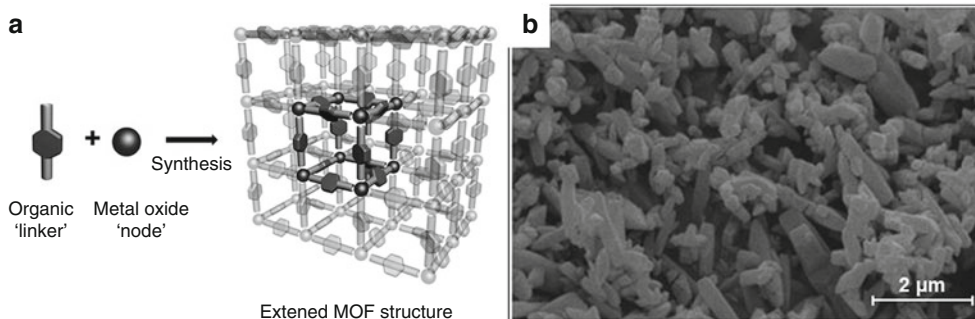
Metal-organic frameworks (MOFs), also called porous coordination polymers (PCPs), are a class of crystalline solid materials whose structure consists of a regular, two- or three-dimensional network of metal cations or metal oxide clusters (so-called nodes) connected by organic molecules (so-called linkers). Figure 1a depicts conceptually how the three-dimensional structure of a MOF is built by assembling metal (oxide) nodes and organic linkers, while Fig. 1b shows a representative scanning electron micrograph of MOF crystals. First reports on metal-organic frameworks date back to 1959 (Kinoshita et al. 1959). Attention toward this class of materials was boosted in the 1990s by more rational approaches to their “reticular” design and synthesis (Hoskins and Robson 1989). Since then,

extensive research efforts have led to several thousand experimentally reported MOF structures and have notably broadened the scope of their potential applications (MacGillivray 2010; MacGillivray and Lukehart 2014). Generally MOFs are synthesized in solution by reacting a salt of the metal node precursor with the organic linker (precursor) molecules. Conventionally, the driving force for reaction, nucleation, and crystal growth is provided by convective (or microwave) heating. Alternatively, electrochemical and mechanochemical synthesis methods, among others, have been described (Stock and Biswas 2012). The MOF crystal size and morphology can be modified by adjusting the synthesis conditions to alter the relative rates of nucleation and crystal growth processes or to favor growth along certain crystallographic directions.

The internal structure of MOFs displays high mass-specific surface areas (typically in the range of 300–6000 m²/g). It typically defines pores and cavities in the micropore range (<2 nm) or, less often, in the mesopore range (2–50 nm). Owing to the large surface areas and porosities, along with their amenability to be designed with adjustable surface properties and pore sizes, in the range of molecular dimensions, via either the judicious selection of the node and linker building units or post-synthesis modifications, MOFs have been long considered ideal solid adsorbents for separation applications.

The capacity of MOFs to separate molecules is generally ascribed to either one or an interplay of several of the following main mechanisms:

1. The “molecular sieving” effect, by virtue of which certain molecules are prevented from penetrating the pores of the MOF while other molecules can enter and adsorb, depending on their molecular size and/or shape.
2. Selective adsorption based on adsorbate-surface interactions, whereby certain intrinsic properties of the molecules such as their polarity or capacity to establish H-bonds determine different adsorption strengths on the surface of the MOF and therefore the preferential adsorption of certain compounds over others. In certain cases, the selective adsorption of a given



Metal-Organic Frameworks (MOFs), Fig. 1 (a) Schematic representation of how an extended MOF structure is built upon the assembly of metal (oxide) nodes and organic linkers (Adapted from image courtesy of Dr. Christian

J. Doonan (University of Adelaide)). (b) Representative scanning electron micrograph of $\text{NH}_2\text{-MIL-53 (Al)}$ MOF crystals

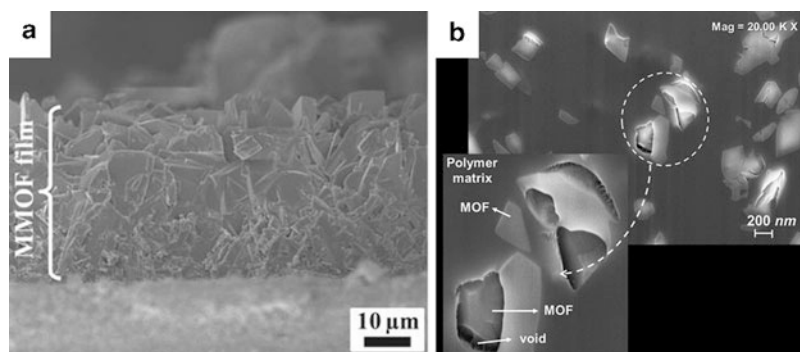
molecule is favored owing to its distinct capacity to adopt an energetically favored packing on the surface of the MOF adsorbent via not only adsorbate-surface but also adsorbate-adsorbate interactions.

3. Adsorbate-induced framework rearrangements. A number of MOF structures exhibit flexibility, i.e., the capacity of their framework to rearrange upon the uptake of certain adsorbates. Strong interaction of the MOF surface with an adsorbate can contract the framework, resulting in a narrower pore aperture. On the contrary, the framework of certain MOFs can expand when the uptake of an adsorbent surpasses a given threshold, giving rise to a wider pore aperture. The latter is widely known as “gate-opening” effect. Such dynamic MOF structural modifications are often highly selective to certain adsorbates and play a determinant role in the discrimination of molecules via either “molecular sieving” or selective adsorption.

As a result of their outstanding potential for molecular discriminations, metal-organic frameworks are considered a prominent example of solid adsorbents for separation applications both in the gas phase and in the liquid phase (Li et al. 2012). Fine-tuning of the pore size/geometry via either direct synthesis or surface modifications has resulted in MOF materials

capable of discriminating even between stereoisomeric molecules, i.e., those having an identical bond of constituent atoms but differing in the orientation of these atoms in space. Attesting their large potential as functional materials for separation applications, MOF synthesis has recently reached industrial scale (http://www.chemistryviews.org/details/news/861963/1st_Industrial-scale_MOF_Synthesis.html).

MOFs can be applied in adsorption-desorption separations, to which end they are shaped in the form of macroscopic pellets or coated on pre-shaped monoliths or meshes. They have also been explored as constituents of membranes (Pera-Titus 2014). On one hand, continuous, thin-film, pure MOF membranes can be prepared by depositing or growing MOF crystals on a porous substrate, as illustrated in the cross-sectional scanning electron membrane micrograph included in Fig. 2a. On the other hand, *composite* or mixed-matrix membranes incorporating MOF crystals as filler material embedded within a polymer matrix have recently attracted a substantial interest as they potentially combine the easy fabrication and processing of polymeric membranes with the intrinsic molecular discrimination properties of MOFs. Figure 2b (bottom) depicts a FIB-SEM micrograph of the internal cross section of a mixed-matrix membrane incorporating discrete MOF crystals within a continuous polymer matrix.



Metal-Organic Frameworks (MOFs), Fig. 2 (a) Cross-sectional scanning electron micrograph of a membrane incorporating a thin film of MOF crystals on a porous α - Al_2O_3 substrate (Adapted with permission from Ranjan and Tsapatsis (2009), copyright (2009) American Chemical Society). (b) Scanning electron micrograph of an internal cross section, exposed upon milling with a focused ion

beam, of a mixed matrix membrane. MOF crystals appear as lighter objects on the darker gray background corresponding to the polymer matrix (Adapted from Rodenas et al. (2014)). The bottom-left inset shows a close-up detail where the different components and boundary voids have been labeled

Cross-References

- [FIB-SEM Tomography](#)
- [Mixed Matrix Membranes \(MMMs\)](#)

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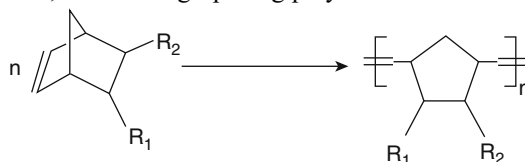
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Metathesis Norbornene Polymer-Based Membrane Materials

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Norbornene and its derivatives are strained bicycles, so their ring-opening polymerization



is thermodynamically favored, so the reaction proceeds easily and with high yields. Numerous metathesis polynorbornenes with different side groups have been prepared and their gas permeation parameters studied (Finkelshtein et al. 2011; Yampolskii 2010). Purely

hydrocarbon polynorbornene has relatively low gas permeability ($P(\text{O}_2) = 2.8$ Barrer). Introduction of one or two bulky nonpolar SiMe_3 groups results in significant increase in gas permeability: the values of $P(\text{O}_2)$ are 30 and 95 Barrer, respectively. On the other hand, appearance of a compact and polar CN group leads to reduction of gas permeability: $P(\text{O}_2) = 0.53$ Barrer. The cis/trans configuration of the double bonds of metathesis norbornene polymers affects gas permeability; the highest values are observed for cis/trans ratio close to unity. The appearance of double bonds in the main chains decreases chemical stability of the polymers: especially unstable is non-substituted metathesis polynorbornene. On the Robeson diagrams, the data points characteristic for various metathesis polynorbornenes are located below the upper bounds, so these polymers are not attractive materials for gas separation. However, their studies provided much information on structure–property relations of potential membrane materials.

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Microalgae Concentration

Carles Torras Font

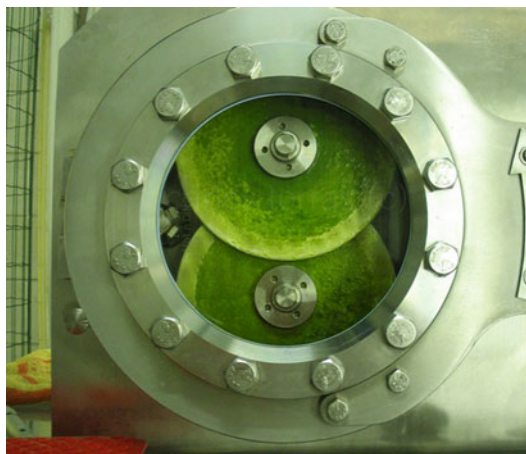
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Second-generation biofuels are those obtained from feedstocks, which their main characteristic is that they do not compete with food industry (Schenk et al. 2008). One of these feedstocks is microalgae (Chisti 2010). This biomass is highly considered nowadays because of other several advantages: microalgae offer a rapid growth,

they possess high lipid contents, marine as well as freshwater species can be used, etc. (Miao and Wu 2006; Rosenberg et al. 2008).

The process to produce biodiesel from microalgae comprises several steps: microalgae cultivation, microalgae concentration, cell disruption, lipid extraction and purification, and transesterification (Chisti 2007). They imply a significant cost, which makes the process economical unfeasible if only biofuel is going to be obtained (Amer et al. 2011). Thus, other products such as nutritional, cosmetic, or pharmacological ones may be considered as well as alcohols (Harun et al. 2010). Considering several products to be obtained responds to the biorefining concept. A bottleneck in the biorefining process deals with microalgae concentration. In the previous step (cultivation), concentrations usually below 1 g/L are obtained, which is approximately 1,000 ppm. Thus, to obtain dry biomass, the major part of the volume should be removed, achieving a reduction of an order of magnitude of 3. There are several techniques that can be applied to concentrate microalgae. Classic ones are sedimentation, filtration, and centrifugation (Molina Grima et al. 2003). Sedimentation is the cheapest one, but it consumes time or flocculants and only achieves a concentration factor between 2 and 4 approx. (which is significant) (Şirin et al. 2011). Centrifugation is the most effective method, but it is also the one that consumes more energy. In the past years, membrane filtration has gained attention due to advances in this technology.

Due to the size of the microalgae cells (almost all above 1 μm), microfiltration can achieve complete rejection of the biomass, and low transmembrane pressures may be used (which is an advantage to minimize the energy needed). Also, the medium is chemically low aggressive to the membrane. Because of these conditions, low-cost membrane materials may be used. But a main problem of using membrane filtration in microalgae concentration is the severe fouling that occurs, which dramatically reduces permeability (Rickman et al. 2012). Decrements up to 99 % have been measured (Rios et al. 2011). Research is currently being performed to reduce the mentioned phenomena. Some works



Microalgae Concentration, Fig. 1 Rotatory membrane filtration setup containing membranes after a microalgae concentration experiment

demonstrated that ultrafiltration may be suitable to reduce this effect (Zhang et al. 2010). Other works propose the use of dynamic systems, which enhances the shear stress over the membrane, and promising results have been reported, reducing fouling significantly (Fig. 1). Also, combination of sedimentation and membrane filtration improves performance (Ríos et al. 2012). Other noticeable works are being performed regarding submerged membrane systems (Bilad et al. 2012), in which cultivation and concentration is being performed simultaneously.

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Microcapsule Membranes

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Definition

Microcapsule is defined as a hollow microsphere comprising large interior void and semipermeable

shells. The interior void serves as storage space or reaction chamber, while the shell protects the bioactive materials/nanoparticles in the interior void from the attack of surrounding environment or controls the transfer of substance in/out the microcapsule. Till now, microcapsule with single shell, double shells, and multiple shells as well as yolk-in-shell structure has been designed and prepared. Since the shell of the microcapsule often possesses nanometer/micrometer thickness and distinct semipermeable property, it fits the typical features of membrane. Therefore, microcapsule shell can be also called **microcapsule membrane**, which was first introduced by Chang in 1960s (Chang 1964).

Characteristics

Microcapsule membrane can be categorized into inorganic, organic, and inorganic–organic hybrid membranes based on the material composition. Inorganic microcapsule membrane usually possesses porous structure and high mechanical stability, which is often synthesized under relatively harsh conditions (e.g., hydrothermal treatment, calcinations, or organic solvent treatment). In comparison, the synthesis of organic microcapsule membrane (mainly self-assembly of amphipathic polymer, layer-by-layer self-assembly, or surface polymerization) is often conducted under rather mild conditions; however, the mechanical stability of organic microcapsule membrane is usually much lower than that of inorganic microcapsule membrane as a result of lack of stiff blocks. Recently, incorporating inorganic components/moieties into organic microcapsule membrane has been demonstrated as a facile, generic to enhance the mechanical stability. Moreover, considering the advantage that hybridization could offer new opportunities to create multifunctional materials with unique properties by combining the merits of inorganic and organic building blocks, hybrid microcapsule membrane may win more promising applications in the future.

Microcapsule membrane has single-, double-, or multiple-layered structure. Single-layered

microcapsule membrane is usually composed of homogeneous polymers or inorganics, while double-layered microcapsule membrane is often composed of two separate layers with different kinds of materials. Multiple-layered microcapsule membrane mainly refers to the microcapsule membrane which is composed of multilayers through the alternative deposition/self-assembly of two kinds of oppositely charged polymers, polymer/inorganic hybrids.

Microcapsule has been applied in diverse areas, including biocatalysis, drug delivery, pollutants removal, biosensing, etc., where microcapsule membrane plays the crucial role in governing the overall performance of the microcapsule. For instance, Jiang et al. prepared protamine–titania hybrid microcapsule membrane and encapsulated the biocatalyst enzyme in the capsule lumen. The enhanced recycling stability of enzyme was due to the high mechanical stability of microcapsule membrane (Jiang et al. 2009). Caruso et al. developed a redox-responsive microcapsule membrane and encapsulated hydrophobic cargo in the capsule lumen. The cargo could be released in simulated intracellular conditions, which were ascribed to reversible disulfide linkages of membrane materials (Yan et al. 2011). Kreft et al. designed a light-responsive microcapsule membrane and encapsulated dextran in the capsules. The dextran is released when near-infrared laser light illuminated the capsules, which was ascribed to the incorporation of light-absorbing gold nanoparticles into the microcapsule membrane (Kreft et al. 2007). Li et al. reported that the porous MnO₂ microcapsules showed good ability to remove an organic pollutant (azo dye Congo red) in wastewater, which was ascribed to the excellent dye adsorption capability of porous microcapsule membrane (Fei et al. 2008). Yu et al. prepared polymeric microcapsule membrane and encapsulated rhodamine 6G. The capsules rapidly released rhodamine 6G in ethanol but cannot release in aqueous solution. This was because the charge density of microcapsule membrane in ethanol was markedly decreased due to its low dielectric constant as compared to that in aqueous solution (Yu et al. 2009).

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Microcapsule Production by Membrane Operations

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Microencapsulation is the technology of packaging individual particles of solid, liquid, or gaseous materials in capsules in the micrometer to millimeter range, which can release their contents at controlled rates or under specific conditions (Chabala et al. 1978). Upon microencapsulation, liquid and gaseous materials are more easily handled since they acquire a solid-like form; it may also afford extra protection, owing to the barrier around hazardous materials.

Processes of microencapsulation have traditionally been categorized into two groups: chemical and physical (or mechanical) processes (Prasad and Sarkar 1992). Indication of which category is at stake may come from whether the

microcapsules are produced in a liquid-containing tank as in chemical processes, as opposed to physical processes that employ a gas phase. There are in practice seven major methods of microcapsule production: coacervation, interfacial polymerization, phase separation, spray drying, fluid bed coating, centrifugal extrusion, and rotational suspension.

Coacervation takes advantage of the reaction between aqueous solutions of cationic and anionic polymers, e.g., gelatin and Arabic gum; such polymers form a concentrated, complex phase called coacervate – which maintains an equilibrium with a dilute supernatant phase. As the water-immiscible core material is introduced into the system, thin films of coacervate coat the dispersed droplets of core material, which are then solidified – thus conferring a harvestable form to the capsules (Klaassen and Jansen 2001). This is probably the most common method of microencapsulation (Ocak et al. 2011); its major advantage is the very high payload (up to 99 %) and controlled release possibilities (Jun-Xia et al. 2011).

The method of interfacial polymerization is characterized by membrane formation via rapid polymerization of monomers at the surface of the particles of (dispersed) core material. A multifunctional monomer is accordingly dissolved in the core material, and this solution is dispersed in an aqueous phase; a reactant with the monomer is added to the aqueous phase, so polymerization quickly ensues at the surfaces of the core particles to eventually form the wall. This method is appropriate for preparation of bigger microcapsules, although the commercial size ranges are 20–30 mm and 3–6 mm.

Phase separation is generally grouped with other chemical encapsulation techniques, despite realization that no actual chemical reaction is usually involved in the process. It utilizes two polymers soluble in a common solvent, but which do not mix with each other in solution; hence, they form two separate phases – one rich in the polymer intended to form the membrane, and the other rich in the incompatible polymer meant to induce phase separation. The latter will not be a part of the finished microcapsule membrane, except for traces caught inside the capsule as impurities.

During spray drying, an emulsion is prepared by dispersing the core material (usually an oil or active ingredient immiscible with water) into a concentrated solution of membrane material until the desired size of drops is attained. This emulsion is then atomized into a spray of droplets by pumping the slurry through a rotating disk into the heated compartment of a spray drier: the water portion of the emulsion consequently evaporates, thus yielding dried microcapsules of variable shape and containing scattered droplets of core material. The microcapsules are finally collected via continuous discharge from the spray-drying chamber.

Fluid bed coating is restricted to encapsulation of solid core materials, including liquids absorbed into porous solids. Such particles are suspended on a jet of air and then covered by a spray of liquid coating material; the microcapsules are then moved to an area to allow solidification of their membranes via cooling or solvent vaporization. The process of suspending, spraying, and cooling may be iterated until the walls attain the intended thickness. When the spray nozzle is located at the bottom of the fluidized bed of particles, the process is usually known as the Wurster process.

Centrifugal extrusion processes generally lead to microcapsules of a larger size, typically from 250 μm up to a few mm. The core and membrane materials (which are supposed to be immiscible) are pushed through a spinning two-fluid nozzle; this procedure forms an unbroken rope that naturally splits into round droplets directly after clearing the nozzle. The continuous walls of these droplets are solidified either via cooling or by a gelling bath depending on the composition and features of the coating material.

When applying the rotational suspension separation (or spinning disk) method, the internal phase is dispersed into the liquid wall material – and the mixture is admitted onto a turning disk. Droplets of pure membrane material are thrown off of the rim of that disk – along with discrete particles of core material enclosed in a skin of wall material. After solidification by cooling, the microcapsules are collected separately from the particles of membrane material.

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Microcapsules

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Microcapsules are discrete portions of an aqueous medium (core) suspended in another aqueous medium, with immiscibility (and hence stability) being assured usually by a lipid layer (membrane) that resembles the phospholipid bilayer of cell membranes. They are often spherically shaped with a continuous membrane surrounding the core, but may take asymmetrical shapes – e.g., with a number of smaller droplets of the core material embedded throughout the microcapsule; microcapsules may also have one or multiple walls around the core, arranged in strata of varying thickness. The core – i.e., the encapsulated substance – has also been termed active ingredient, nucleus, or internal phase; the membrane – i.e., the encapsulating material – is also referred to as coating or wall (Jyothi et al. 2009).

The purpose of microencapsulation is to confine the core material within the capsule membrane and

protect it. Alternatively, core materials may be encapsulated so that they will be released gradually through the membrane (known as controlled release or diffusion) or when release is intended to occur after a given period of time – upon a change in external conditions that trigger the wall to rupture, melt, or dissolve. Microcapsules can be classified, according to the type of membrane, as slow release, impermeable, and smart (Jackson and Lee 1991).

In the case of slow-release membranes, the encapsulated component is released from the capsules for a longer time, depending on the final usage intended therefore. The release time depends on the membrane type – in particular its composition and thickness – and may vary from few days to several months (Marini et al. 1991). The core component may be water- or solvent-based and may assume a solid or a liquid state. Applications that regularly resort to such a type of membrane are fragrances and flavors, pesticides, and reactive chemicals. An example of the former is chewing gum – in which flavors are supposed to last longer than the first bites. Another example is when flavorings are comprised of two reactive components that should not react and thus lose their flavor potential prematurely; in this case, the two components are microencapsulated individually. Pesticides are also encapsulated to bring about release over time, thus allowing farmers to apply them less often and at lower (and thus less toxic) concentrations than in a single use; the environment is better protected, and a more efficient strategy for pest control results. Many varieties of oral and injected pharmaceutical formulations are microencapsulated as well – not only to effect release of the active component(s) over a longer period of time but also to guarantee release only at certain locations in the body. One example is aspirin, which can cause peptic ulcers and bleeding if doses are introduced all at once: slow release decreases its detrimental risks on the stomachal mucosa (Arshady 1993).

Impermeable membranes have the active component encapsulated inside the membrane; the chief purpose is to prevent release and thus

assure complete isolation from the environment. This solution has been proven useful for phase change materials targeted at textile and building industries: the said materials absorb or release heat in response to changes in environmental temperatures – when temperatures rise, they melt thus absorbing excess heat and causing a sensation of cool; conversely, as temperatures fall, phase change materials release heat as they solidify, thus providing a sensation of warmth. This unique property of microencapsulated phase change materials can be harnessed to increase the comfort level of users of sports equipment and military clothing; they have even been used in NASA-patented thermal protection systems for spacecraft. Additionally, the use of impermeable membranes is useful in retaining volatile flavors: encapsulation extends the shelf life of the food product, by retaining flavors that would otherwise evaporate and be readily lost.

Finally, when the core substances should be released only in certain circumstances (e.g., when pH or temperature changes or when exposed to mechanical forces), smart membranes are selected. Successful examples are microencapsulated fragrances that operate on the principle of scratch and sniff for release and some flavorings that must be protected from oxidation caused by exposure to light – so they should not be released prior to mastication (Obeidat 2009).

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Microchannel Emulsification

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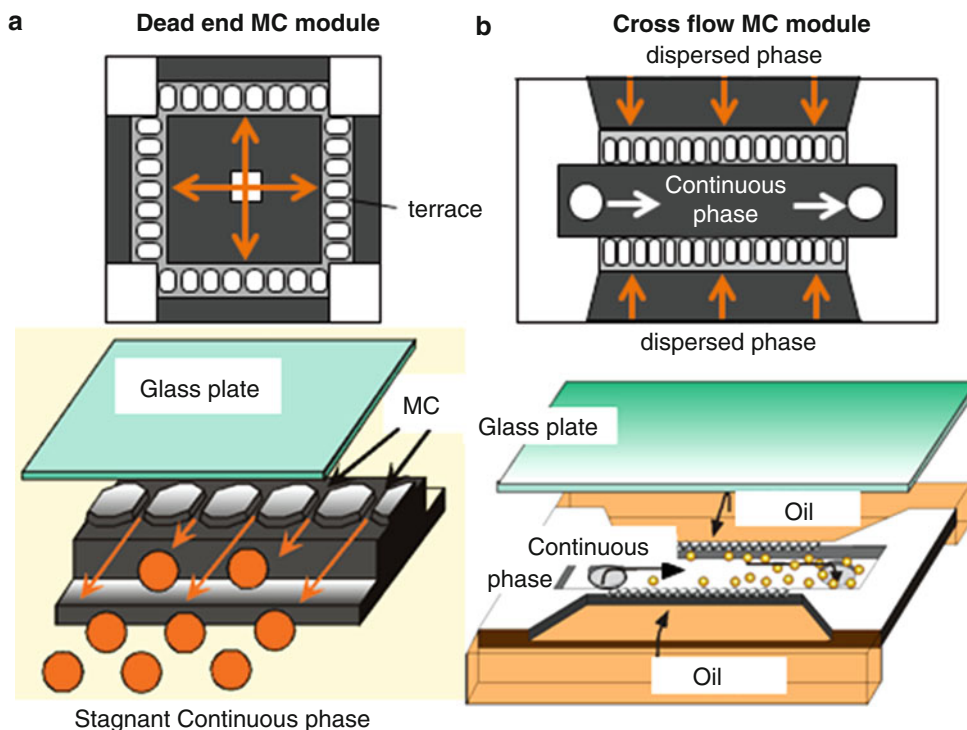
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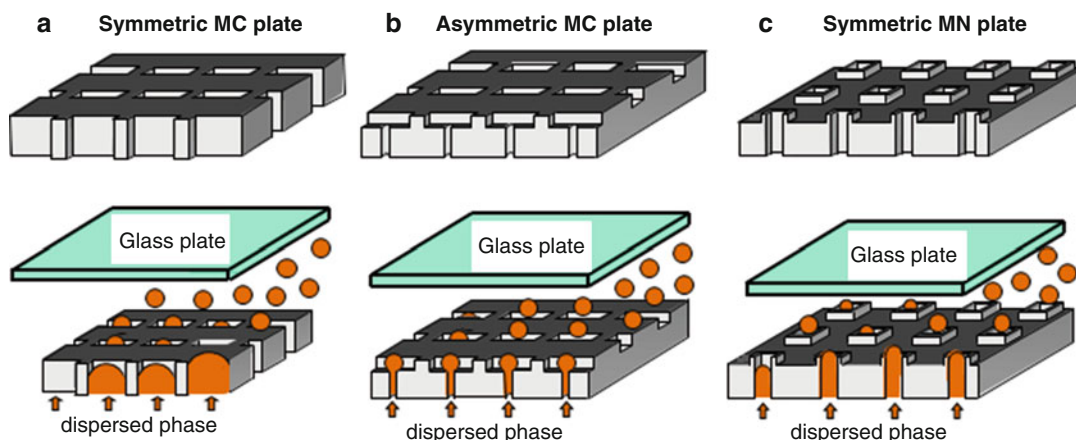
Microchannel (MC) emulsification is a process of forming emulsions by injecting a dispersed phase through a multitude of microfabricated MC arrays into the continuous phase. Single-crystal silicon MC arrays can be fabricated in the form of horizontal grooves (Kikuchi et al. 1992) or vertical straight-through holes (Kobayashi et al. 2002).

Grooved-type MC plates are fabricated by photolithography and anisotropic wet etching and can be used in dead-end or cross-flow configuration. In a dead-end module (Fig. 1a), parallel grooves fabricated on a terrace are arranged on all four sides of the plate. The dispersed phase supplied through a central hole is forced to flow through MCs, because the plate is sealed with a transparent cover plate. The dispersed phase takes a disklike shape on terrace, and this shape is characterized by a higher interfacial area per unit volume than a spherical shape, resulting in hydrodynamic instability. This instability is a driving force for spontaneous transformation of dispersed phase into spherical droplets (Sugiura et al. 2002).

Dead-end modules provide a dispersed phase flow rate less than 0.1 mL h^{-1} , due to limited number of MCs (less than 2,000). Cross-flow modules with grooved MC arrays are suitable for higher production scales because multiple cross-flow channels with MC arrays can be incorporated on a single plate (Kobayashi et al. 2010). The



Microchannel Emulsification, Fig. 1 Grooved-type MC plates for MC emulsification (Published with permission from Vladisavljević et al. 2012)



Microchannel Emulsification, Fig. 2 Straight-through MC plates for MC emulsification (Published with permission from Vladislavjević et al. 2012)

simplest cross-flow module (Fig. 1b) has only one cross-flow channel and two holes at its both ends for introduction and withdrawal of the continuous phase. The purpose of cross flow is to collect droplets from the module and not to control the droplet size. In the dripping regime, the droplet size is independent on the flow rate of dispersed or continuous phase. Cross-flow MC plates with multiple cross-flow channels are available with a maximum cross section of 60×60 mm and 12,000 MCs arranged in 14 parallel arrays (Kobayashi et al. 2010).

Modules with grooved-type plates have a limited throughput, because MCs are arranged on the plate surface in longitudinal direction, and feed channels for the dispersed and continuous phase are provided on the plate surface. A vertical array of straight-through MCs fabricated by photolithography and deep reactive ion etching allows better utilization of the plate surface resulting in significantly higher throughputs. Straight-through MCs may have a symmetric and asymmetric structure. Symmetric MCs (Fig. 2a) are of the same size and shape (e.g., circular or rectangular) along the whole cross section of the plate. Rectangular MCs provide higher droplet size uniformity than circular MCs, and an aspect ratio of the slots should be at least 3 (Kobayashi et al. 2004). Asymmetric MC plate has circular channels on the upstream (bottom) side and slots on the

downstream (top) side (Fig. 2b). Asymmetric plate is useful when the dispersed phase viscosity is less than 1 mPa s, e.g., when the dispersed phase is a volatile hydrocarbon (Kobayashi et al. 2005). Straight-through micronozzle (MN) array (Fig. 2c) are used to increase the velocity of continuous phase around the growing droplets during detachment, because the channel outlets are above the plate surface, which could be useful if the viscosity of the dispersed phase is high (Sugiura et al. 2005).

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Microencapsulation Synonym: Microentrapment

► Encapsulation Application

Microfiltration (MF)

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General

Microfiltration (MF) is a pressure-driven membrane-based process separating suspended solids and fine particulates in the range of 0.1–10 μm from liquid. The vast size range covers a wide variety of industrial and natural compounds and particles. Microfiltration is able to effectively remove colloids, microparticles, microorganism, and macromolecules from suspensions. The efficiency and cost of microfiltration depends on permeability measured as flux and selectivity tabulated as rejection. Numerous factors affecting these two vital parameters including membrane characteristics

(material, morphology, and pore size) and operating parameters such as transmembrane pressure, cross-flow velocity, and feed properties (concentration, temperature, pH, ionic strength, surface chemistry).

The efficient microfiltration is widely utilized in food and beverage industries, biotechnology, and water and wastewater treatment to significantly remove turbidity, bacteria, and protozoa from water and wastewater. Moreover, several published studies reported partial virus removal by MF (Madaeni et al. 1995).

This technology has several advantages including high selectivity, high product quality, fast operation, small space requirement, continuous and fast operation, ease of scale-up, low running costs, and moderate capital investment. Moreover, microfiltration processes are compatible with the environmental standards due to no formation of by-product and limited usage of chemical additives.

Theoretical approaches are able to predict the performance of microfiltration process using appropriate models including mass transfer, osmotic pressure, gel polarization, boundary layer adsorption, Brownian diffusion, shear-induced diffusion, inertial lift, and surface transport models. The estimation limitations are complexity of mathematical equations, requirement of experimental data for verification, prediction for steady-state flux only, and validation for certain feed and conditions.

Applications

Microfiltration is widely employed for filtering numerous varieties of particles including microorganisms such as algae, fungi, protozoa, bacteria, and viruses.

Viruses are roughly ten times smaller than the pores of microfiltration membranes, i.e., they are small enough to pass through the membranes. However, it has been demonstrated (Madaeni et al. 1995) that hydrophobic microfiltration membrane with the pore size of 220 nm is capable to

remove poliovirus with the size of 20 nm significantly (greater than 99 %). Similar results were found for animal viruses such as FMD and IBR (Madaeni et al. 2013).

Although ultrafiltration membrane is able to completely retain the viruses, the main benefit for microfiltration membrane is higher flux. Virus removal depends on membrane characteristics including surface properties and interfacial properties of viral particles. An appropriate membrane structure, i.e., thick multilayered with porous structure, improves the virus trapping capacity. Moreover, interactions of viruses with the surfaces of membranes improve the removal efficiency. This includes electrostatic and hydrophobic interactions. High retention is obtained with a hydrophobic membrane compared to hydrophilic due to the hydrophobic interaction. Preconditioning of the virus suspension influences the removal capability. Aggregation around the isoelectric point of a virus or in the presence of salt improves the rejection of viruses. The aggregation is significantly improved by manipulating the ionic strength and pH of the feed.

The top priority aim in water treatment is finding new techniques to produce water without formation of by-product and with limited usage of chemicals. This can be achieved by microfiltration which is used to remove suspended solids from water and wastewater. Membrane technology is able to meet the needs for higher productivity and lower cost in biotechnology.

Oily wastewaters containing surfactants, cosurfactants, various additives such as antifoaming agents, and bactericides are among the major environmental pollutants which require purification for reuse and protection of the environment. The conventional procedures exhibit disadvantages including low efficiency, high-energy consumption, high operation costs, and corrosion. Moreover, sometimes the non-reacted chemicals are found in the final wastewater. Microfiltration has been employed for successful treatment of oily wastewaters using both polymeric and ceramic membranes. The latter may be applied at elevated temperature, harsh

chemical environment with uncomplicated regeneration procedure.

Considerable quantities of water, after industrial and domestic use, are discharged in rivers, lakes, and sea. Very often the discharged water causes pollution of surface and underground water. Membrane processes are among the purification techniques to significantly reduce the volume of the polluted water.

In wastewater treatment, controls of discharges require superior solutions compared to conventional biological treatment. One possible solution is the replacement of a secondary sedimentation by suspended microorganisms on the surface of a microfiltration membrane. When large particles like microbial flocks are present in the wastewater, a layer of microorganisms is accumulated on the membrane surface which is known as dynamic membrane.

Microfiltration with many applications in food industry can be used in fruit juice clarification, dairy applications, selective separation of micellar casein, fractionation of milk fat, removal of whey fat, cheese brine purification, separating whole milk into cream and skim milk, and sterilization by reducing bacterial level. The separation of bacteria, spores, yeast, and molds from milk by microfiltration has been further confirmed.

However, membrane fouling and consequent flux reduction due to precipitation of available feed components in membrane pores or on membrane surface are the major obstacle for wide utilization of membrane separation in general and microfiltration in particular.

Hybrid Processes

In addition to direct application of microfiltration membrane, a possible way for improving the process performance is to combine membrane with conventional techniques as hybrid systems. In many cases, the improved hybrid system is able to carry out the desired separation and/or provides higher efficiency compared to the sum of individual stages.

A few examples are presented here. An outstanding application of microfiltration is sterilization of temperature-sensitive solutions such as biologic liquids. However, microfiltration membranes are not able to remove all microorganisms from a solution. Moreover, nano-silver particles exhibit antibacterial capability. Membrane combination with nano-silver results in complete sterilization of the feed (Madaeni and Akbarzadeh Arbatan 2010).

Around 6-log reduction can be achieved for the removal of bacteriophages (bacterial viruses) using microfiltration membrane in combination with coagulation. Microfiltration membranes in combination with bacteria may be employed for degradation of organic contaminants, heavy metals, and inorganic materials in wastewater. The elimination efficiency depends on the specifications of bacteria (type, activity, and surface property) and membrane. Some bacteria such as *Pseudomonas putida* are able to treat heavy metal pollution in industrial sewages or degrade organics, e.g., toluene. For higher removal efficiency, membrane can be coupled with lime as a coagulant for the precipitation of heavy metals, NaOH, and ion-exchange resin. The hybrid process of activated carbon and microfiltration utilizes the capability of activated carbon to adsorb impurities and the ability of membranes for removal of microorganisms and particles.

The integrated membrane systems based on combination of microfiltration and other membrane process such as ultrafiltration or nanofiltration can be conducted for efficient purification and/or as a pre-filtration step for minimization of system's fouling.

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Microfiltration Membrane

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General

The core of microfiltration process is a thin (10–1,000 μm) porous (0.1–10 μm) polymeric or ceramic membrane. The detailed morphology or structure and physical and chemical characteristics or properties of the membrane influence the separation capability.

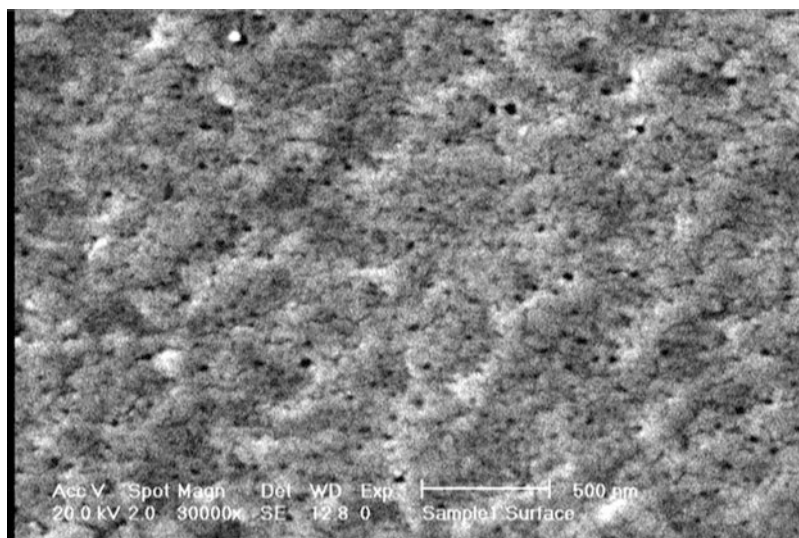
Electron microscopy images of surface and cross-section of a membrane are widely accepted for visualization of membrane structure. The membrane surface may change from a smooth to a rough appearance. The membrane pores are extensively varied from hole-like pores (Fig. 1) to tortuous openings (Fig. 2). The shapes and sizes of the membrane pores are greatly changed depending on the point by point preparation procedures and conditions.

The membrane consists of two distinct parts (Fig. 3). The thin (around 1 μm) skin layer is the main segment conducting the separation process and the thick (around 100 μm) support provides mechanical stability. In many cases an intermediate layer exists between the two main layers. The skin layer includes tiny membrane pores. The very large openings in the support do not primarily influence the separation capability. The main limitation for large or small pores in the support is mechanical stability. However, recent studies indicate that any part of the membrane including support may have impact on the membrane performance (Madaeni et al. 2012).

The membrane characteristics and morphology affect the performance. This includes but not limited to the characteristics of membrane material (polymer, ceramic), pores (size and shape), surface (charge, smoothness), preparation procedures and conditions, etc.

Microfiltration Membrane,

Fig. 1 Surface of microfiltration membrane showing the hole-like pores

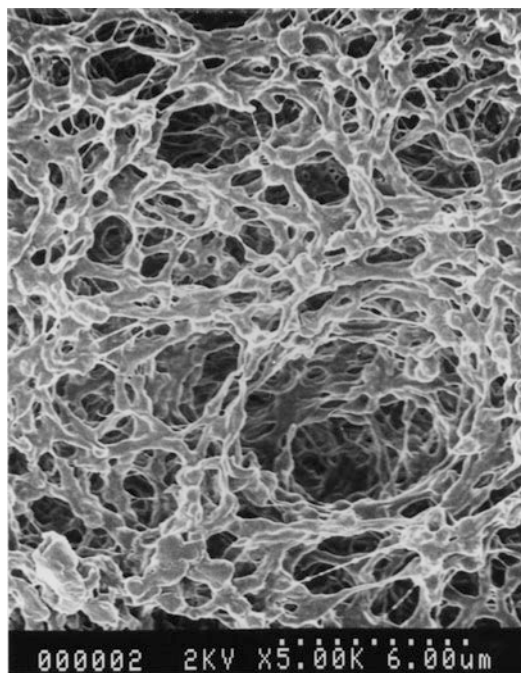


Microfiltration membranes are used for treatment of water containing particles, colloids, oil, and microorganisms, sterilization of liquids by reducing bacterial level, clarification of fruit juice, purification of cheese brine, separation of pharmaceutical materials, fractionation of milk, removal of whey fat, etc.

Membrane Preparation

Microfiltration membranes are generally prepared on the basis of classical methods such as phase inversion via various procedures including immersion precipitation, track etching, stretching, etc. Control of membrane morphology is significant for obtaining acceptable permeability, selectivity, and mechanical strength. Permeability reveals the productivity, selectivity exhibits separation capability, and the latter indicates the limitations regarding applied pressure and flowing fluid throughout the membrane.

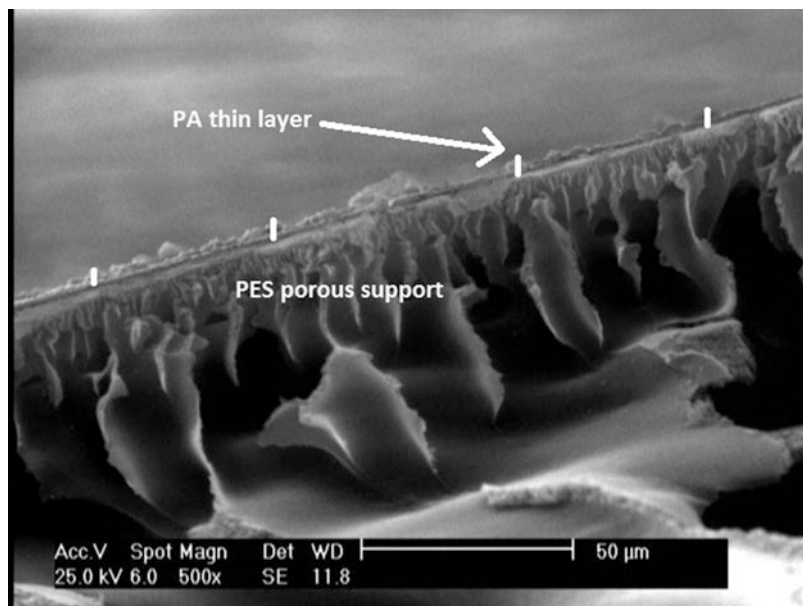
The parameters affecting the manufacturing process are numerous. Neglecting a part of the influencing factors results in variation in membrane structure and characteristics leading to inconsistency in membrane performance. There is a strong relationship between membrane preparation and membrane properties. Membrane materials (both base and additives) and



Microfiltration Membrane, Fig. 2 Surface of microfiltration membrane showing the tortuous pores

preparation conditions are major concerns. The parameters which must be monitored and controlled during manufacturing process include but not limited to the characteristics of membrane main material, additives and casting solvent,

Microfiltration Membrane, Fig. 3 Cross-section of microfiltration membrane showing thin layer and support



coagulation medium type, precipitation temperature, details of the preparation procedure, and conditions such as temperature (both recipe and environment), pressure, humidity, required time for each step, etc.

Slight manipulating the affecting parameters greatly influences the membrane characteristics. For instance, evaporating the volatile solvent in dope solution before immersing in the coagulation bath improves the membrane structure. Membrane pore size is reduced by increasing the evaporation time. Moreover, the evaporating step is able to prevent the membrane shrinkage in the coagulation bath and suppress the formation of macrovoids leading to mechanical breakdown. It has been shown (Madaeni et al. 2012) that the casting thickness intensively affects the membrane morphology and macrovoid formation. Influence of the coagulation bath temperature and evaporation time on membrane morphology depends on the temperature difference between the coagulation bath and the casting solution (Madaeni et al. 2012).

Although both polymeric and ceramic microfiltration membrane are in use, similar to other types of membranes, polymeric membranes are more common. A widely used polymer for manufacturing microfiltration membranes is

polyvinylidene fluoride (PVDF). This is due to excellent chemical resistance and good thermal and mechanical properties. The polymer is acid resistant, chemically inert, semicrystalline polymer containing crystalline, and amorphous or rubbery phases. Thermal stability and flexibility are provided by the crystalline and the amorphous phases, respectively. PVDF is readily dissolved in many solvents but is stable against corrosive chemicals including acids, alkaline, and oxidants.

Membrane Modification

Microfiltration membranes may be modified after preparation to convert the existing membrane to a new one with enhanced characteristics. Nowadays, this is the main procedure for obtaining superior membranes. The modification techniques are developing and may be considered as a hub for researches in the field of membrane manufacturing. The methods include but not limited to surface treatment (coating, grafting, radiation), functionalization of membranes with appropriate chemical groups, and introduction of nanoparticles into the membrane recipe or onto the membrane surface.

For instance, surface modification of PVDF membrane was conducted using 8-hydroxyquinoline

Microfiltration Membrane,

Fig. 4 Deposition of particles on the surface and inside the pores of microfiltration membrane

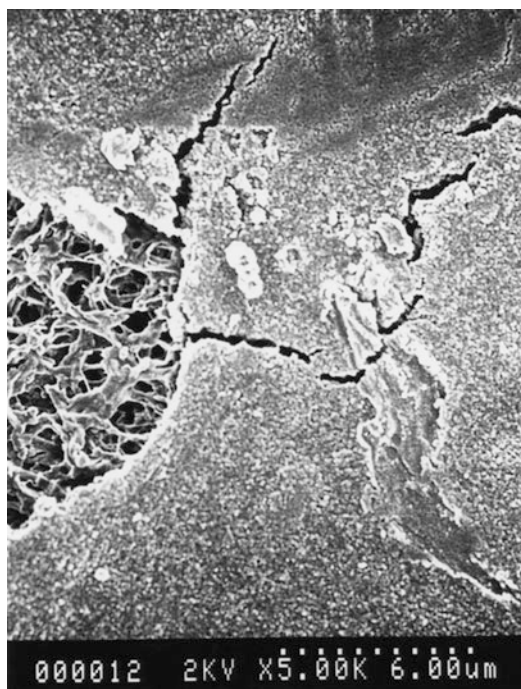


(Madaeni and Heidary 2012). The introduced functional group interacts with hydroxyl group of PVDF membrane due to the hydrogen-bond interaction. The interaction is chemically stable. This chelating agent forms sparingly soluble derivatives with metallic ions. The modified membrane can be employed for the removal of cadmium and nickel from water.

Fouling

The main obstacle for application of membranes is fouling. This is due to the deposition of feed components on the membrane surface or in the membrane pores (Fig. 4). The precipitation of particles gradually leads to formation of a cake layer (Fig. 5). Fouling results in flux decline (lower productivity) and rejection alteration (lower selectivity). The most important fouling tackles are characterization, mechanism, and procedures for fouling minimization.

Using cross-flow mode can reduce fouling by deposition limitation on the membrane surface. In addition, the tangential shear depending on the velocity of the suspension is able to remove the foulant layer. The cake deposition on various parts of the membrane is inconsistent. This has been confirmed by SEM micrographs and CFD modeling (Madaeni et al. 2010).



Microfiltration Membrane, Fig. 5 Cake layer formation on the surface of microfiltration membrane

Chemical cleaning is considered as the most important method for regeneration of fouled membrane. The type of cleaning agent depends on the properties of the fouling layer. In many cases the optimum chemical cleaner is elucidated

by trial and error. The choice of cleaning agents is extensive for ceramic membranes.

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Microfiltration Membrane Bioreactor

► Aerobic Membrane Bioreactor

Microscale Modeling and Membranes

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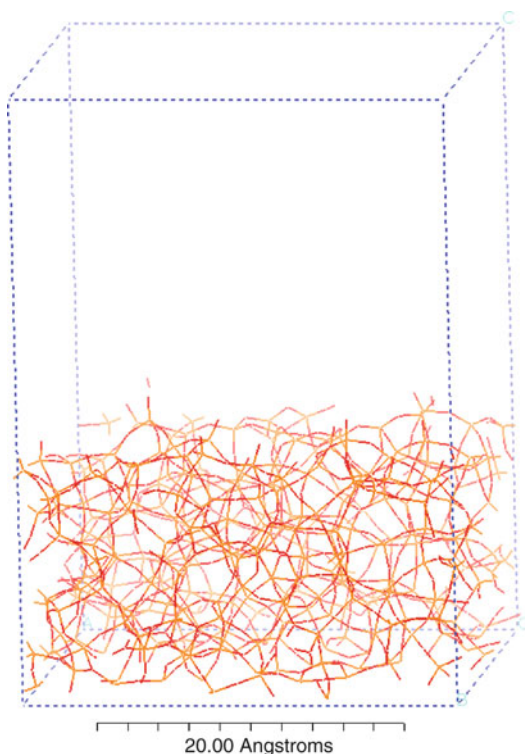
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Microscale modeling refers to the modeling of membrane processes at a resolution level where fundamental phenomena can be described with minimum assumptions using first principles. Modeling tools at the microscopic level usually encompass molecular dynamics (MD) and/or Monte Carlo (MC) techniques, which incorporate many degrees of freedom for the detailed analysis of transport, sorption, reaction, and other process phenomena in membranes. Because of the tremendous significance of the internal structure of

membranes on their performance, especially in separation or preferential transport applications (e.g., fuel cells and membrane reactors), models of the membrane structure at the microscopic level have been developed. In *polymeric*, “rubbery” membranes, models of gas transport in their interior are mainly based on free volume concepts. In the free volume approaches, the concentration dependence of the penetrant diffusivity is described by considering the average spaces between chains (Flory 1969). Such models commonly relate the mutual diffusion coefficients for a gas/polymer system to the free volume of the system. Significant efforts have been made to explain the mechanisms of gas transport in polymers by means of molecular theories. Molecular theories attempt to analyze the diffusion process in terms of specific postulated motions of the polymer chain relative to each other and the motion of penetrant molecules. In order to move into the polymer matrix, the gas molecule pushes the polymer chain and jumps into a new position (Pace and Datyner 1979). At around the glass transition temperature and below, thermal fluctuations of the polymer configurations are limited and penetrants are assumed to jump between cavities with a motion that is likely to entail a significant activation energy barrier (Crank and Park 1968). Simulations in glassy polymers have been attempted with the help of a dual-mode sorption model and some free volume model description. Attempts have also been made to explain gas diffusion in polymers by various molecular mechanisms and models that involve the calculation of the energy for an assumed specific simplified polymer conformation after an energy-activated jump of the penetrant. Most models are leading to the concept of available free volume as diffusing channels (Kotelyanskii and Theodorou 2004). In fact, the mechanism of gas separation by *dense, nonporous membranes* is different from that by porous ones, since diffusion occurs via a *solution-diffusion* mechanism; the permeants dissolve in the membrane material and then diffuse through the membrane down a concentration or chemical potential gradient. Separation between the different permeants is achieved due to differences in the amount of material diffusing through the

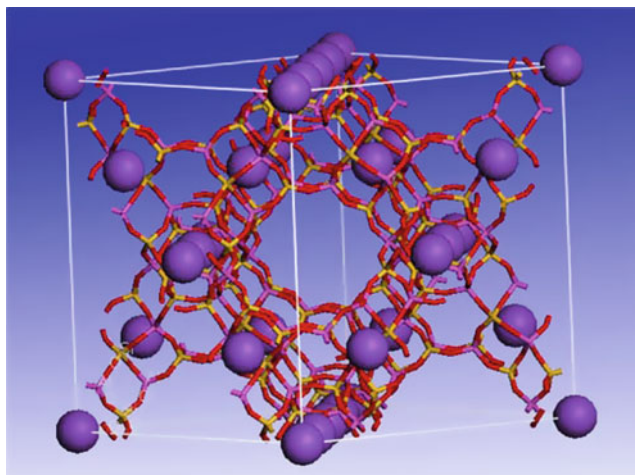
membranes. The microstructure of membranes, both polymeric and inorganic, used in *gas separation* is usually reconstructed at the atomistic level, to study the interaction effect of solute or diffusing molecules with the membrane material.



Microscale Modeling and Membranes,
Fig. 1 Atomistic reconstruction of SiO₂ (Accelrys Material Studio)

The reconstruction of *inorganic* membrane structures at the molecular scale is usually realized using MD and MC techniques. Initially, the atoms of the membrane materials are positioned at predefined bulk lattice sites, taken from literature, experimental data, or diffraction techniques. The interatomic potential energy of the configuration is dynamically calculated using some force field description. The force field approach involves an analytical expression that gives the energy of a molecular system in terms of the positions of all its atoms. Both intramolecular (short) and non-bonded (long) atomic interactions are usually taken into account. These data are obtained using either empirical or quantum mechanical (QM) calculations. Using a force field, useful quantities such as momenta, interaction energies, conformational energy barriers, and free energies can be estimated. The atomistic structure is the basis for MD and MC calculations to probe the locations, conformations, and motions of molecules, predicting the actual supply of sorbates to the active sites of membrane (Allen and Tildesley 1987). Mesoscopic and macroscopic membrane process parameters, such as permeabilities, diffusivities, sorption isotherms, reaction and decay coefficients, as well as (perm) selectivities, used in mesoscopic simulations derived from kinetic theory, Fickian, or Stefan-Maxwell (dusty gas) approaches, can then be derived based on proper integration of their microscopic origins (Figs. 1 and 2).

Microscale Modeling and Membranes,
Fig. 2 FAU structure with equilibrated Na⁺ cations (Accelrys Material Studio)



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Microsolute

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Microsolute represents an operational term which denotes any diffusible (able to pass through a membrane) solute(s) in a solution that also contains nondiffusible (retained by membrane) solute(s), macrosolute. Membrane filtration may be used to treat such solution to recover microsolute which is valuable from solution or to filter microsolute which is regarded as impurity out of the solution.

Distinction of species considered as microsolute depends on membrane process which is used to treat the solution (Cheryan 1998), in the case of:

- Microfiltration – Microsolute is represented by macromolecules and species with smaller particle sizes.
- Ultrafiltration – Microsolute represents dissociated acids, divalent salts, sugars, and species with smaller particle sizes.
- Nanofiltration – Undissociated acids and monovalent salts can be recovered or filtered out.
- Reverse osmosis – Only water passes through membrane and thus can be considered as microsolute.

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Microwave Synthesis of Zeolite Membranes

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Microwave synthesis of zeolite membranes applies microwave irradiation to the synthesis of zeolite membranes as heat source. Microwave technique is regarded as a novel tool in chemical synthesis which offers enhanced speed, reproducibility, and scalability compared to conventional heating. The pioneer work on microwave synthesis of zeolites can be traced back to 1988, and work on zeolite films and membranes subsequently began in the late 1990s. Microwave heating usually combines with two hydrothermal synthesis strategies: in situ synthesis and secondary (seeded) growth. So far, LTA, MFI, AFI, FAU, SOD, T, ETS-4, et al. types of zeolite membranes have been successfully synthesized with the assistant of microwave heating (Li and Yang 2008). LTA zeolite membrane is most extensively studied among them and achieves scale-up to produce commercial zeolite membranes (Xu et al. 2000; Li et al. 2006).

Microwave synthesis of zeolite membranes can have certain benefits over conventional synthesis methods:

1. Shorter synthesis time with higher energy efficiency
2. Uniform crystal size and facile morphology control
3. Improved membrane compactness with higher membrane selectivity
4. Easier for scaling up

It is generally accepted that microwave heating mainly owes its superiority to being instantaneous, volumetric, and selective, known as “thermal effects.” Some researchers suggest the existence of “nonthermal effects,” even in liquids, which are supposed not to require the transfer of microwave energy into thermal energy. For microwave synthesis of zeolite membranes, nonthermal effects are still part of an ongoing debate. Some speculations of the nonthermal effects are proposed for microwave synthesis of LTA zeolite membranes (Li and Yang 2008). In their opinion, the acceleration effect of microwave synthesis is mainly due to the thermal effects, whereas the distinctive morphology of LTA zeolite membranes synthesized by microwave is due to the nonthermal effects.

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Milk Fat Hydrolysis

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Milk contains ca. 3.4 % total milk fat – which has probably the most complex fatty acid profile of all edible fats. Despite the over 400 individual fatty acid residues identified, only 15–20 account for 90 % of milk fat: saturated

(4:0, 6:0, 8:0, 10:0, 12:0, 14:0, 16:0, and 18:0), monounsaturated (16:1 and 18:1), and polyunsaturated (18:2 and 18:3). Some of these fatty acids are found to be in very low levels, but they are also characterized by very low odor thresholds – so they contribute unique and desirable flavor keynotes.

Milk fat can be degraded chiefly by oxidation upon exposure to light and hydrolysis in the presence of enzymes; these two chemical processes follow quite different chemical mechanisms. Enzymes able to hydrolyze fat are called lipases (or glycerol ester hydrolases, EC 3.1.1.3), and the process is often referred to as lipolysis. These enzymes possess a catalytic triad similar to those in proteases but along evolution have developed a portion of the peptide chain into a lid that covers the active site – which opens (and thus permits access to substrate) only when a water/lipid interface is present; this unique feature makes their action distinct from that of classical esterases in that they are activated by lipids in emulsified form.

Lipases suitable for modification of milk fat – toward incorporation into baked goods and the like – are commercially obtained from a range of sources: milk (lipoprotein lipase), pancreas (pancreatic lipase), molds (e.g., *Aspergillus niger*, *Geotrichum candidum*, and *Penicillium roqueforti*), bacteria (e.g., *Achromobacter lipolyticum* and *Pseudomonas fluorescens*), and the gastrointestinal tract (kid and lamb pregastric esterases). Several genetically engineered microorganisms may also produce such enzymes, both in endogenous and exogenous forms (Fox and McSweeney 1998).

Lipases also have the ability to catalyze the reverse of hydrolysis – i.e., ester synthesis, under microaqueous conditions. These two basic processes may then be combined in a sequential fashion to lead to interesterification reactions. The underlying catalytic mechanism resembles closely natural metabolic pathways, so lipase-based processes are viewed as more environment friendly than typical bulk chemical syntheses. Because of their low activation energies, lipase-mediated processes require mild temperature and

pH, so energy consumption is small and there is little thermal damage to either reactants or products. Owing to their chemical selectivity and stereoselectivity, lipases may generate high added-value products that are not readily available in natural feedstocks.

The essential manufacturing steps of hydrolyzed (or lipolyzed) milk fat include: preparation of condensed milk or butter oil, preparation of standardized lipase system in water, combination of milk fat substrate and lipase system, homogenization to form a stable emulsion (thereby promoting maximum interfacial enzyme activity), incubation at controlled temperature (until a specified degree of hydrolysis has been achieved), pasteurization (to completely inactivate residual lipase), and final standardization, spray drying (or alternative formulation), and packaging.

Controlled enzymatic hydrolysis of milk fat has been a common practice in the dairy industry to produce butter- or cheese-like products and flavor additives (Walstra et al. 1999). The intrinsic composition of lipolyzed milk fat can indeed impart a range of effects on the sensory profiles of foods: at very low addition levels, a sensation of richness is obtained without any detectable acidity; as addition levels increase, the resulting flavors resemble cream or butter; and when addition levels are even higher, the outcome flavor suggests cheese.

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Milk Microfiltration

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Membrane-based technologies, in particular pressure-driven membrane processes, have been assuming an increased importance in milk and milk whey processing over the last 40 years. Microfiltration (MF) is a membrane separation process that uses porous membranes with average pore diameters within 0.1 and 10 μm . Therefore, MF membranes are capable of retaining particles, cells and large macromolecules (e.g., polymers), finding diverse applications in dairy industry, such as for the removal of bacteria (Ribeiro et al. 2011), whey defatting (Goudédranche et al. 2000) and the production of concentrates enriched in casein micelles.

In alternative to thermal treatment and centrifugation, milk pasteurization can be performed using MF, which also assures an extended milk shelf life (Kosikowski and Mistry 1990; Ribeiro et al. 2011). MF allows for an efficient removal of bacteria from milk, preventing simultaneously the activity of microbial enzymes, which are released by dead cells remaining in milk upon thermal treatment (Saboya and Maubois 2000). Moreover, MF allows milk processing, i.e., pasteurization and clarification in cold conditions, thus avoiding thermal-induced protein aggregation (Beaulieu et al. 1999). Therefore, MF minimizes the inconvenient alteration of texture and the loss of organoleptic and nutritional properties of milk and milk derivatives (Kosikowski and Mistry 1990) that may result from protein aggregation or post-pasteurization enzymatic activity. Proteins are structurally sensitive to heat, forming aggregates, e.g., β -lactoglobulin and k-casein aggregates, at high temperatures (Beaulieu et al. 1999) which may generate the undesirable depletion of these compounds from milk by precipitation or upon centrifugation. In particular, the reduction of casein content is an important drawback in cheese

industry since it retards the rennet coagulation (Singh and Waungana 2001).

Besides cold milk pasteurization, MF potentiates the development of dairy-based products (e.g., cheeses, butters) with diverse and optimized properties (Daufin et al. 2001). Indeed, MF allows the controlled adjustment of milk ingredients through adequate selection of process conditions (e.g., membrane pore size, transmembrane pressure, temperature). Milk pretreatment with MF generates two different process streams: a retentate solution enriched in casein (casein micelles) that may be used in cheese manufacturing for improvement of the coagulation process and a permeate stream, containing a significant concentration of valuable dairy components, such as sugars (e.g., lactose), whey proteins, and bioactive peptides. Whey proteins, such as α -lactalbumin, β -lactoglobulin, lactoferrin, immunoglobulins and growth factors, have important nutraceutical properties and, as well as the bioactive peptides, are relevant ingredients in food and health applications. The recovery of these compounds either as protein whey concentrates (WPC) or isolates (WPI) came along with the development of ultrafiltration (UF) membranes in later 1970s and 1980s. UF allows the fractionation of milk whey into their isolated components or fractions enriched in a specific target protein, allowing their judicious application as enhancers of product quality according to their particular properties.

The use of pressure-driven membrane processes at an industrial scale has been hampered by membrane fouling problems resulting from a time-dependent deposition of solutes at the membrane surface and within the pores. In dairy processing, membrane fouling is mainly attributed to the deposition of particles, like fat globules and cells, and also it is importantly influenced by protein-protein (protein aggregates) or protein-membrane (protein adsorption) interactions (Velasco et al. 2003). In this context, MF may be used for milk whey pretreatment in order to alleviate fouling intensity in UF and NF processes, which may be used for the recovery of milk whey added value compounds and/or for the reduction of the organic charge of the dairy industry

wastewaters. Membrane fouling causes the apparent decrease of membrane average pore size, leading to the reduction of permeate fluxes, the progressive change of membrane selectivity and consequently the production of process streams with undesirable composition. Membrane fouling is intimately dependent on the process hydrodynamic regime, the membrane module design and the physicochemical characteristics of the processing media (Velasco et al. 2003). Therefore, the process productivity and the product quality results from a combined effect of these factors. Optimal solute separation is generally achieved at subcritical transmembrane pressures (TMPs) where membrane-fouling phenomena and flux decline are not observed (Field et al. 1995). However, if purity is not the main process criteria, such as in bacteria removal by MF, then it is preferable to use TMP slightly above the critical value in order to improve permeate fluxes and hence the process productivity. Additionally, long-term process performances are benefited by operation under minimal fouling conditions, which are achievable by using operation strategies involving soft and uniform TMP conditions (Sandblom 1974).

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Milk Protein, UF Application of

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Milk is composed of a large diversity of proteins with high nutritional value, specific bioactive properties, and physiological functions. Caseins, including α -casein, β -casein, and γ -casein, are the major milk protein components, representing ~80 % of the total milk protein content (Eça and Ferreira 2006). Caseins have low solubility in the aqueous phase, and therefore they are found in micelle form as a colloid component of milk. Besides caseins, milk contains an important amount of water-soluble proteins, the milk whey proteins, composed of β -lactoglobulin (7–12 %), α -lactalbumin (2–5 %), β -lactoglobulin, serum albumin (0.7–1.3 %), immunoglobulins (1.9–3.3 %) and a minority group of proteins with important bioactivity composed of lactoferrin and lactoperoxidase among others (Eça and Ferreira 2006).

Milk whey is the effluent resultant from cheese production mainly comprised of lactose (79 g/L), mineral salts (5.6–8.4 g/L), and whey proteins (8.4 g/L) (Suárez et al. 2006). Whey contains an important organic load (high chemical oxygen demand, COD, values), and therefore it cannot be discarded into the environment without

previous treatment. Moreover, despite being a rich source of nutraceutical compounds with important physiologic functions, its high salinity disallows its use for animal feed purposes. The use of membrane processes has a dual benefit in milk whey treatment; it allows the reduction of the whey COD content towards the production of a clarified waste stream (Balannec et al. 2005) with physicochemical characteristics that fulfill the requirements for its disposal or reuse. Simultaneously, membrane processes allow for a selective recovery of the added value ingredients, such as lactose or proteins, into fractions enriched in a specific(s) compound(s). Nanofiltration (NF) and reverse osmosis (RO) must be used for an efficient removal of mineral salts and sugars (Catarino et al. 2008; Minhalma et al. 2007), whereas protein fractionation is achieved by ultrafiltration (UF) processes (Van Eijndhoven et al. 1995). The development of UF membranes was driven by the emerging interest in a selective recovery of milk proteins envisaging their use as enhancers of specific product properties. UF membrane pore sizes are within the range of protein molecular size, thus varying between 1 and 500 kDa. UF membranes are classified according to their molecular weight cutoff (MWCO), which expresses their ability to reject 95–97 % of compounds with a specific molecular size. The UF fractionation of milk whey proteins into pure solutions of each specific protein is difficult and hampered by the presence of non-uniform membrane pore sizes, by the ability of proteins to permeate through pores with a MWCO smaller than their molecular size, and also by the presence of membrane fouling. Protein permeation through pores narrower than its molecular size is explained by protein structural adaptability to confined spaces and by the protein structural changes potentially induced by the permeation process (Portugal et al. 2008), e.g., due to the shear stress conditions to which proteins may be exposed during permeation or protein-membrane interactions. Additionally, the progressive deposition of proteins at the membrane surface and within the membrane pores – membrane fouling – leads to changes of membrane selectivity and permeability, resulting in alterations of the chemical composition of the

Milk Protein, UF Application of, Table 1

Description and content of the main proteins present in skimmed milk (Adapted from Eça and Ferreira 2006)

	Proteins	Protein content in skimmed milk (%)
Caseins	α -S ₁ -casein/ α -S ₂ -casein	45-55
	β -casein	25-35
	k-casein	8-15
	γ -casein	3-7
Milk whey proteins	β -lactoglobulin	7-12
	α -lactalbumin	2-5
	Bovine serum albumin (<i>BSA</i>)	0.7-1.3
	Immunoglobulins (<i>IgG₁, IgG₂, Ig A, Ig M</i>)	1.9-3.3
	Lactoferrin	0.2-0.8
	Lactoperoxidase	-

product. Protein transmission is largely influenced by protein-protein (Saksena and Zydney 1997) and protein-membrane interactions. Attractive protein-protein interactions generate the presence of protein aggregates, thus altering their effective molecular size and consequently amplifying protein rejection. High protein-membrane affinity improves protein adsorption at the membrane surface, leading to higher membrane fouling and a higher decline of flux permeation. Therefore, protein transmission can be controlled by suitable adjustment of the physicochemical properties of the processing media, namely, pH and salt concentration (Nystrom et al. 1998; Menon and Zydney 1999), through modulation of attractive and repulsive protein-protein and protein-membrane electrostatic interactions. Protein transmission through UF membranes and membrane selectivity depend crucially on the processing parameters used. High selective separations are promoted by the selection of membrane with adequate pore sizes and by using moderate permeation fluxes. Hence, protein fractionation processes are benefited by operations under controlled permeate flux since it allows for a better control of the permeate flux at subcritical

conditions, thus reducing the membrane fouling potential (Howell et al. 1998; Crespo et al. 1999).

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Mineralization

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Mineralization in water is the complete breakdown of organic substances with the end products being CO₂, H₂O, and nutrients. If organic compounds contain heteroatoms such as nitrogen, chlorine, phosphate, sulfur, etc., the complete mineralization by oxidation will release inorganic ions like ammonium, nitrate, chloride, orthophosphate, and sulfates, respectively. Production of CH₄ can also be considered as part of the mineralization process because it comes up in parallel to the minerals in methanization.

Mineralization can be the result of a biological or chemical oxidative process in which organic substances are converted to inorganic substances. When referring to membranes, measuring mineralization rate is a way to estimate efficiency of catalytic membrane reactors.

The mineralization rate of organic pollutant in water can be measured by total organic carbon

analyzer (TOC) or chemical oxygen demand (COD) with some restrictions. The evolution of total organic carbon (TOC) is then a measure of the extent of mineralization (Rivas et al. 1998).

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Mixed Conducting Membranes

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Synonyms

Electronic and ionic conductivity

A mixed conducting membrane can transport both electrons and ions as shown in the scheme below (Fig. 1); in most cases the ionic conductivity is based on oxygen ions or protons, but in principle also other ions like halogenide or chalcogenide anions are mobile and can be transported. Perovskites with the crystallographic structure ABO₃ (derived from the mineral perovskite CaTiO₃) are a prominent example for a materials class with mixed conductivity: Oxygen ions can be transported via vacancies in the oxygen lattice (denoted as oxygen deficiency δ in the perovskite structure ABO_{3- δ}), and electrons can be transported via redox cycles of the cations if they can occur in different oxidation states (e.g., Feⁿ⁺, Coⁿ⁺, Tiⁿ⁺). The concentration of vacancies in the oxygen lattice can be engineered by bringing cations with a low valency on the position of high-valency cations (Sunarso et al. 2008).

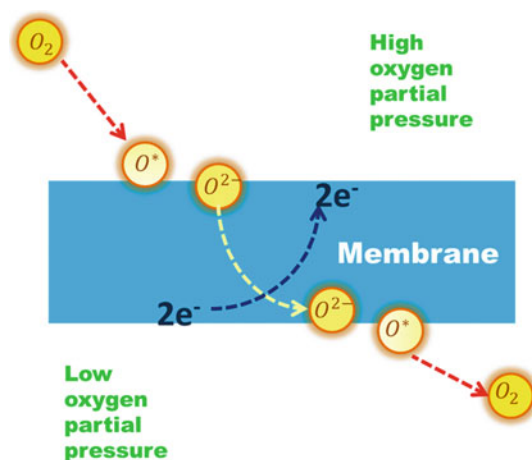
In contrast to mixed conducting membranes, the membranes used in fuel cells for electricity

generation show only ionic conductivity: In the solid oxide fuel cell (SOFC), the membrane material such as $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-8}$ (CGO) shows only oxygen ionic conductivity and no electronic conductivity, and the electrons have to go therefore an outer circuit, whereas the oxygen ions move through the CGO. In the case of the polymer electrolyte membrane (PEM) fuel cell, the membrane material Nafion shows also only proton conductivity (Grotthuss mechanism) but no electronic conductivity, and also here the electrons have to go an outer circuit, whereas the protons can diffuse through the hydrated Nafion pores.

Therefore, mixed conducting materials are often called materials with an inner shortcut

since oxygen ions and electrons or protons and electrons move through the material.

In the scheme below (Fig. 1), the phenomenon of mixed conductivity is illustrated for a perovskite membrane. On the membrane side with a high oxygen partial pressure (e.g., air), molecular oxygen is split at the surface into atoms, the atoms become ionized, and the oxygen ions occupy empty oxygen ion positions in the oxygen lattice (vacancy) and become transported by a diffusion mechanism to the membrane side with a lower oxygen partial pressure (vacuum, sweep gas) where they back-transform into molecular oxygen. For most perovskites, the electronic conductivity is orders of magnitude higher than the ionic one.



Mixed Conducting Membranes, Fig. 1 Schema of oxygen transport through a perovskite membrane with mixed conductivity (copyright Caro, Uni Hannover): Molecular oxygen is split at the membrane side with high oxygen partial pressure (normally air) into atomic oxygen species O^* which are adsorbed at the surface. After ionization, the oxygen ions O^{2-} enter the mixed conducting membrane material. By a diffusional hopping process among the vacancies in the oxygen lattice, the oxygen ions can enter the membrane side facing a low oxygen partial pressure. Here the reverse process takes place: The oxygen ions decompose into atomic surface oxygen O^* and electrons, and the latter diffuse to the air side where they are consumed in the oxygen ionization. The surface oxygen species O^* dimerize and form molecular oxygen which is desorbed into the gas face. To keep the oxygen partial pressure low on the permeate side (driving force for permeation), the molecular oxygen has to be removed by pumping or a sweep gas; it can be also consumed in a chemical oxidation reaction (Shao et al. 2001)

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Mixed Matrix Membranes (MMMs)

► Nanocomposite Membranes

Mixing Index

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Synonyms

Degree of mixedness

Mixing index is a measure of the degree to which fluid flow will promote the dispersion of dissolved solutes or suspended materials in the fluid, leading to homogeneity. It is an indicator of the quality of the mixing process.

Mixing can be defined as a process that influences a heterogeneous physical system such that it becomes more homogeneous. In fluid systems, mixing leads to heat and/or mass transfer between different locations within the fluid. Mixing is of particular importance at the microscale (from several hundred microns to the nanometer range), where diffusion dominates momentum, heat, and mass transfer (Nam-Trung and Zhigang 2005). Several types of mixing have been identified in fluid systems (Ottino 1989): the mixing of fluids containing dissolved solutes caused by stretching and folding of material, the mixing governed by diffusion and chemical reaction, and the mixing caused by breakup and coalescence of material.

A mixing index can help determine whether mixing is occurring and to what degree. A simple mixing index is the Peclet number (Pe), which is defined as the ratio of convection to diffusion:

$$\text{Pe} = \frac{Ul}{D} \quad (1)$$

where U is the (absolute) fluid velocity, D is the solute diffusivity, and l is a relevant length scale. A possible length scale is the Prandtl length (Plawsky 2001), which is the length of the path a mass of fluid or eddy would travel before losing its individuality by mixing or coalescing with its neighbors. A large Peclet number means convection dominates and more mixing is taking place.

Studies of mixing strategies often evaluate the extent of mixing enhancement which is produced in addition to the mixing intrinsic to the original flow field. For this purpose, it is common to use the perturbation velocity vector $\mathbf{u}$, rather than the absolute velocity $\mathbf{U}$, to quantify mixing. The kinetic energy of the perturbation, referred to as the “turbulent kinetic energy” (κ), is a simple measure of mixing:

$$\kappa = \frac{1}{2} \int_{\Omega} \|\mathbf{u}\|_F^2 dV \quad (2)$$

where Ω is the volume of fluid under analysis and $\|\mathbf{u}\|_F$ is the Frobenius norm of the perturbation velocity vector. However, kinetic energy itself is not sufficient for effective mixing. Mixing caused by material stretching and folding can be quantified through the stretching length based on the gradient of perturbation velocity (Ottino 1989):

$$S = \int_{\Omega} \|\Phi\|_F^2 dV \quad (3)$$

where $\Phi = [\nabla \mathbf{u} + (\nabla \mathbf{u})^T]/2$ is the stretching tensor. A mixing estimation parameter that uses the vorticity to describe mixing induced by vortices can also be defined (Alexiadis et al. 2007). Defining $\Psi = [\nabla \mathbf{u} - (\nabla \mathbf{u})^T]/2$ as the folding tensor, mixing related to folding can be quantified through

$$\mathcal{F} = \int_{\Omega} \|\Psi\|_F^2 dV \quad (4)$$

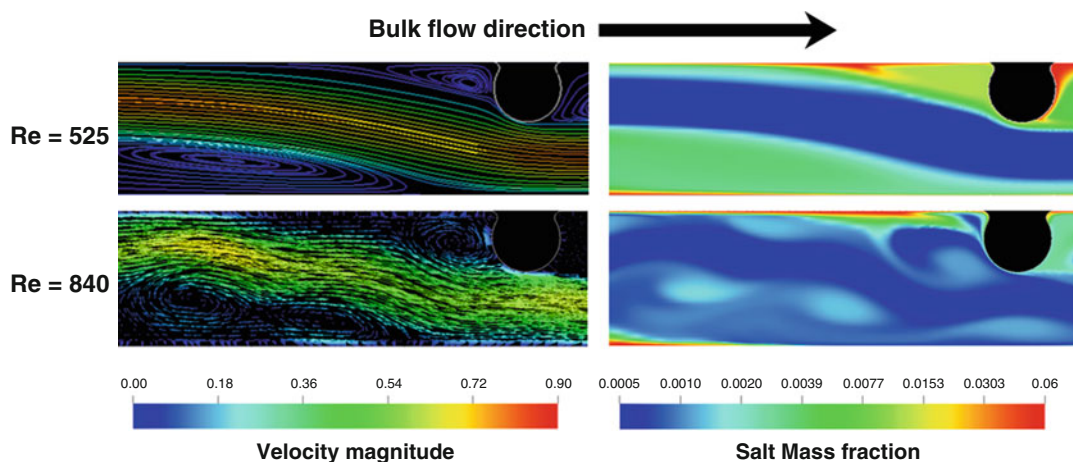
The sum of perturbation-induced stretching and folding can also be used as a mixing index (Balogh et al. 2005; Ouyang et al. 2013) and is expressed as

$$\mathcal{M} = S + \mathcal{F} = \int_{\Omega} \|\nabla \mathbf{u}\|_F^2 dV \quad (5)$$

The mixing indices defined by Eqs. 3, 4, and 5 describe mixing enhancement due to perturbations but do not reflect mixing inherent in the steady-state system and related to the original velocity gradients and momentum diffusion. The interaction between steady-state flow and the perturbation can also lead to stretching and is described by

$$\Gamma = \int_{\Omega} \{(\mathbf{U} \cdot \nabla) \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{U}\} \cdot \mathbf{u} dV \quad (6)$$

Mixing indices have also been used in the design of control systems that maximize the degree of mixing. Expressions involving turbulent kinetic energy and a measure of spatial gradients of perturbation velocities have been used as cost



Mixing Index, Fig. 1 Examples of mixing caused by flow instabilities in a spacer-filled channel

functionals for optimal flow control problems (Aamo and Krstić 2003). Maximizing these cost functionals leads to mixing enhancement. This has applications for membrane separation systems (Ouyang et al. 2013), as mixing enhancement within the vicinity of the membrane surface leads to an increase in the throughput of the membrane system (Fimbres-Weihs and Wiley 2008).

In membrane systems, mixing can be caused by mechanical inserts, by laminar flow instabilities such as oscillating flow or eddy flow, or by turbulent flow (Winzeler and Belfort 1993). Instabilities can be promoted through flow obstacles (eddy promoters) such as the spacers that keep membrane leaves apart, membrane surface modifications, rotating membranes (Couette flow), curved channels (Dean vortices), pulsating flow, and electroosmotic flow. Figure 1 shows examples of flow instabilities caused by spacer mesh filaments in a membrane channel. At the lower Reynolds number of 525, the stationary recirculation region causes mixing behind the spacer filament, but this leads to accumulation of solute within the recirculation region and, hence, poor mixing. At the higher Reynolds number of 840, vortex shedding occurs, leading to more fluid stretching and folding and therefore better mixing within the channel.

Cross-References

- [Diffusive Transport](#)
- [Mass Transfer Resistance](#)

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Mobile Carrier

Gerardo León

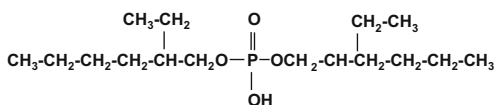
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Mobile site carrier. Solute transport and selectivity in liquid membranes is enhanced by the use of compounds, known as carriers, which reversibly react with the specie to be separated, facilitating its transport (carrier-mediated transport). Although the use of fixed carriers has been described (Lacan et al. 1995), mobile carriers are more frequently employed. Fixed carrier technique implies binding the carrier within the membrane solid matrix, either by electrostatic forces, as in the case of ion-exchange membranes as supports or by covalent linkages, so that the

reversible reaction between the solute and carrier occurs continuously throughout the thickness of the membrane. The carrier agents have no mobility within the film, but the solute moves between carrier sites.

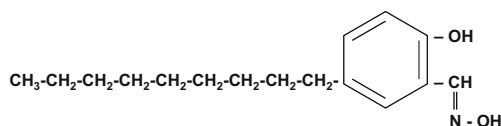
Mobile carrier technique implies adding to the liquid membrane phase a compound (mobile carrier), soluble in the membrane phase but insoluble in the feed and product phases, which reversibly reacts with the solute giving a membrane soluble specie. The mobile carrier diffuses from the bulk membrane phase to the feed membrane interface, where it reacts with the specie to be transported. The formed compound diffuses through the membrane to the membrane product interface where, by reversing the described reaction, the transported specie is released into the product phase. The carrier is regenerated, beginning a new separation cycle. In this way, each carrier molecule is able to transport target specie molecules as many times as necessary, so that only a

Bis-2-ethylhexyl phosphoric acid (D2EHPA)

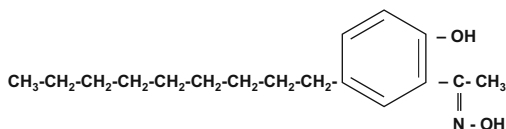


LIX 984N

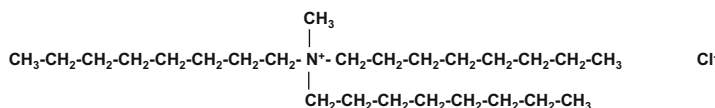
50% 5-nonilsalicyl aldoxima



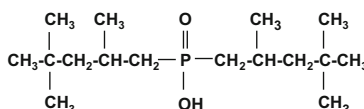
50% 2-hidroxi-5-nonil acetofeniloxima



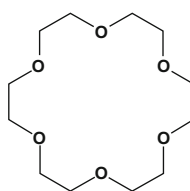
Tri-N-octylmethyl ammonium chloride (ALQUAT 336)



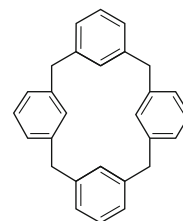
Bis-(2,4,4-trimetilpentil) phosphinic acid (CYANEX 272)



18-crown-6



Calix[4]arene



Mobile Carrier, Fig. 1 Chemical structures and names of different mobile carriers

small amount of carrier is required in the membrane phase even for achieving a high degree of separation. An ideal carrier will possess the following characteristics (Klassen et al. 2005; Kislik 2010):

- high affinity and selectivity for the component to be removed from the feed solution;
- high ability to join to the specie to be removed in the feed/membrane interface (high joining or complexation constant) and high ability to de-join in the membrane/product interface (high de-joining or de-complexation constant);
- rapid kinetics of joining (complexation) and de-joining (de-complexation);
- rapid kinetics of diffusion of the target specie-carrier compound (complex) through the membrane phase;
- formation of a solute-carrier complex that is soluble in the organic solvent; • low solubility in feed and product phases;
- low toxicity and low corrosivity;
- suitable physical properties as density, viscosity, surface tension, etc.;
- easily reused or regenerated;
- no side reactions;
- no irreversible or degradation reactions;
- good chemical stability;
- reasonable price at industrial applications.

Carriers can be classified into three general classes (Ho and Li 1992): acid, basic, and neutral. Acid carriers include chelating compounds (ketoximes, aldioximes, and their mixtures, and β -diketones) and nonchelating compounds (derivatives of phosphorous acids and thioacids, including phosphoric, phosphonic, and phosphinic acids and thioacids and organic acids, such as naphthenic acids). Basic carriers include high molecular weight primary and secondary amines, tertiary amines, and quaternary ammonium salts. Neutral carriers include calixarene derivatives, crown ether derivatives, phosphate and phosphonic esters, and phosphine oxides and sulfides. Chemical structure and names of some of these carriers are included in Fig. 1.

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Modeling of Biocatalytic Membrane Reactor

► [Biocatalytic Membrane Reactor, Mass Transport in](#)

Modified Cellophane Membrane

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Modified cellophane membrane has been obtained through different modification strategies focused on the alternation of the physical and/or chemical characters and structure to have more controlled pore size and shape for final different applications. Craig and Konigsberg (1961) modified cellophane dialysis membrane through mechanical stretching of wet membrane. Such modification will endorse membranes to permeate those solutes which would barely diffuse through native one to pass through at a much accelerated rate. Peterson and Livingston (1964) cross-linked cellophane membrane chemically using starch

dialdehyde to control permeability of potassium chloride ions from dilute solution. Recently, de Lara et al. (2006) have cross-linked cellophane membranes with different cellulose content using gamma irradiation. They found a decrease in diffusional permeability, but slightly effects on the transport of ions across the membrane as a result of a more tight structure. Weber and Nose (1968) modified the cellophane membrane through fiber reinforcement. They found that the reinforced cellophane membrane had superior physical strength, but was inferior to the regular cellophane membrane in urea clearance. Baldwin et al. (1965), Takigami et al. (1979), Nonaka et al. (1997), and Mohy eldin et al. (2009, 2011) investigated the grafting of cellophane membranes with different types of polymers to have functional cellophane membranes for different applications such as ionic barrier for battery, poly-electrolyte fuel cell, hemodialysis, and immobilized metal ion affinity membranes for protein separation. Tomé et al. (2011) modified cellophane membranes' hydrophobic character and barrier effects by controlled heterogeneous esterification with fatty acid derivatives. A decrease in both the water permeation and the permeability toward definite gases in the wet state was observed for the modified membranes.

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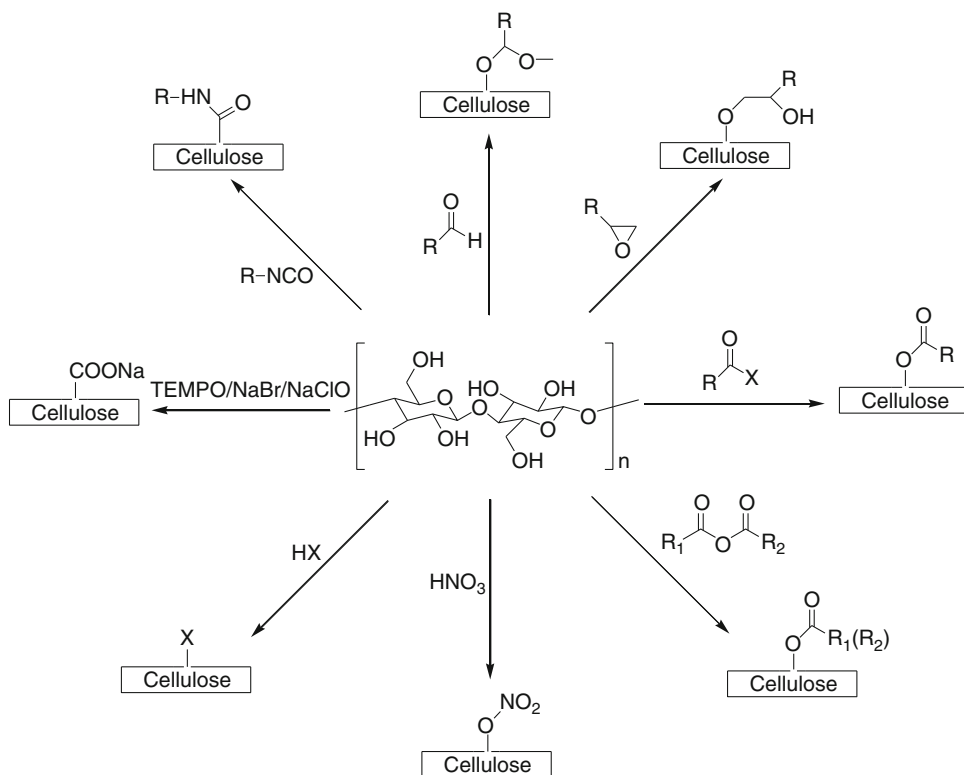
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Modified Cellulose

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Modified cellulose refers to chemical modifications of mainly hydroxyl groups in the cellulose backbone. There are primary and secondary hydroxyl groups in each cellulose unit, where the C6-hydroxyl group, being the primary one, exhibits higher reactivity. Typical reactions of hydroxyl groups in cellulose, including oxidation, esterification, etherification, urethanization, amidation, and non-covalent modifications (Habibi 2014), are shown in Fig. 1.

There are two approaches to modify cellulose for membrane preparation: homogeneous and heterogeneous. A well-known membrane prepared from homogeneously modified cellulose is the cellulose acetate-based reverse osmosis membrane, fabricated by the phase inversion method (Strathmann et al. 1971). Cellulose esters, including nitrocellulose, have also been employed to fabricate commercially available microfiltration membranes by using the phase inversion method



Modified Cellulose, Fig. 1 Chemical modifications of cellulose for membrane science and technology

M

for drinking water purification (Ulbricht 2006). The goals for homogeneous modification of cellulose are to adjust the properties of cellulose for specific applications. However, cellulose cannot be dissolved in common organic solvents. Thus, ionic liquids have been used to dissolve cellulose, thereby expanding the family of homogeneously modified cellulose for membrane fabrication (Ma et al. 2010). Nevertheless, heterogeneous modification of cellulose has, so far, been more frequently used. As an example, cellulose nanofibers extracted from natural cellulose with a heterogeneous oxidation reaction followed by mechanical treatment (Isogai et al. 2011) can afford viable surface modifications. The surface of cellulose nanofibers with a nanoscaled diameter is covered with hydroxyl, carboxylate, and aldehyde groups which can be further modified following the above strategy. Cross-linked cellulose nanofibers with functional surfaces have been used as a barrier layer in micro- and ultrafiltration

membranes for water purification to remove contaminants. These membranes showed superior filtration efficiency when compared with commercial membranes (Ma et al. 2011).

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Modified Fouling Index (MFI)

► Fouling Index

Modularity

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The modularity takes into account the changes of the plant size due to variations of the plant productivity (Criscuoli and Drioli 2007). It is a typical property of membrane operations, since it is possible to add modules, also without having foreseen the expansion of the system in the system design phase.

To compare the modularity of membranes with that of traditional units, a modularity index is defined. Given a variation of the plant productivity (e.g., from productivity₁ to productivity₂), this metric compares the variations of the area (for membranes) with those of the volume (for conventional systems). The membrane system has a higher modularity if the modularity metric is lower than 1; modularity values higher than 1 are in favor of the traditional system.

$$\text{Modularity} = \frac{\left[\frac{\text{Membrane area}_2}{\text{Membrane area}_1} - \frac{\text{Productivity}_2}{\text{Productivity}_1} \right]}{\left[\frac{\text{Conventional unit volume}_2}{\text{Conventional unit volume}_1} - \frac{\text{Productivity}_2}{\text{Productivity}_1} \right]}$$

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MOF

► ZIF-8 Membrane

Molecular Diffusivity

► Diffusivity

Molecular Dynamics in Membranes

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Over the last 30 years, detailed atomistic molecular modeling techniques, namely, the molecular dynamics (MD) and the Monte Carlo (MC), have become a widely used method for the investigation of the molecular structure of membrane materials and transport properties in various membrane operations (Binder 1995; Gubbins and Moore 2010; Hofmann and Tocci 2009; Maginn and Elliot 2010; Theodorou 2006, 2010; Razmus and Hall 1991; Harmandaris and Mavrantzas 2004).

Molecular dynamics simulations have been used to build or modify membranes and to investigate the physical and surface properties of membranes used in gas separation and water treatment processes. The molecular modeling of polymer-based membrane materials generally starts with the construction of typically rectangular packing models (Hofmann and Tocci 2009). There, the related chain segments of the respective polymer are arranged in a realistic, that is, statistically possible, way. The limited lateral dimensions of packing models of just several nanometers make it impossible to simulate complete membranes or other polymer-based samples. Therefore, on the one hand, bulk models are considered that are typically cubic volume elements of a few nanometers side length that represent a part cut out of the interior of a polymer membrane. On the other hand, interface models are utilized, for example, for the interface between a liquid feed mixture and a membrane surface or between a membrane surface and an inorganic filler. The quality of

atomistic packing models is typically validated via comparisons between measured and simulated properties like wide-angle X-ray scattering (WAXS) curves, densities, etc.

Example: Free-Volume Distribution

The free-volume distribution in amorphous polymers is of paramount importance for their transport behavior toward small- and medium-sized penetrant molecules. Atomistic molecular modeling utilizing bulk models on the other hand can provide additional even more detailed information on the magnitude, the spatial distribution, and the connectivity of accessible volume within an amorphous polymer matrix (Theodorou 2010).

The accessible volume for a given penetrant molecule is the volume of the volume domain composed of points that can be occupied by the center of mass of the penetrant without any overlap between the van der Waals spheres of the penetrant and those of the polymer atoms. For most polymer–penetrant pairs of practical interest, the accessible volume in any configuration is partitioned into disjoint clusters.

Generally, for polymeric membranes with low permeability of small molecules, such as diisopropylidimethyl PEEK WC (DIDMPEEK), the accessible free volume is organized in relatively small isolated holes and a size distribution that is monomodal and extending only to hole radii of about 5 Å (Hofmann and Tocci 2009).

Polymers with ultrahigh permeability, such as PTMSP and Teflon AF2400 of DuPont ($\text{PO}_2 = 1,140$ Barrer), show ultrahigh free volume. In this case, simulation data support the existence of a bimodal distribution of accessible volume clusters. One mode of the distribution, with a maximum at around 3–4 Å, is comparable to the distributions encountered in dense glassy, low permeability polymers. The other, in parallel, is a partly continuous phase of much larger holes that in this case are visible as a peak between 15 and 20 Å (Hofmann and Tocci 2009; Jansen et al. 2009).

Examples in Gas Separation: Dense Polymeric Membranes

The permeation of small molecules in amorphous polymers is typically following the solution diffusion model, that is, the permeability P_i of a feed component i can be envisioned as the product of the respective solubility S_i and constant of diffusion D_i . Both parameters can be obtained experimentally and in principle also by atomistic simulations (Theodorou 2006).

The most common approach to obtain diffusion coefficients for gases and vapors is equilibrium molecular dynamics. The diffusion coefficient that is obtained is a self-diffusion coefficient by using the Einstein (Eq. 1) or by means of the Green-Kubo (Eq. 2) formulations:

$$D = \lim_{t \rightarrow \infty} \frac{\langle [r(0) - r(t)]^2 \rangle}{6t} \quad (1)$$

$$D = \frac{1}{3} \int_0^\infty \langle v(0) \cdot v(t) \rangle dt \quad (2)$$

As temperature is reduced toward and below T_g , penetrant diffusion in an amorphous polymer matrix becomes too slow to be predictable by MD simulations. Direct MD would require long simulation times for the prediction of diffusivity in low-temperature rubbery polymers and polymer glasses, which are most relevant from the point of view of membrane and barrier material applications (Theodorou 2006; Fried 2006). In such cases diffusion is considered as a sequence of infrequent penetrant jumps, and the transition state theory (TST) of Gusev et al. (1995) and the multidimensional TST approach developed by (Greenfield 2004) can be utilized. Transport-related diffusion coefficients are less frequently studied by simulation but several approaches using non-equilibrium MD (NEMD) simulation have also been used (Theodorou 2006).

The solubility of gases and vapors can be obtained by means of several computational approaches, principally the Widom particle insertion (Widom 1963) and the Grand Canonical

Monte Carlo (GCMC) (Binder 1995; Theodorou 2006; Razmus and Hall 1991) methods. The interaction energy of a gas particle inserted within the accessible free volume of the polymer matrix is calculated, and the excess thermodynamic potential μ_{excess} can be estimated from (Eq. 3)

$$\mu_{\text{excess}} = RT \ln \langle \exp(-E_{\text{int}}/kT) \rangle \quad (3)$$

The solubility S is then obtained from relation (Eq. 4)

$$S = \exp(-\mu_{\text{excess}}/RT) \quad (4)$$

Also in this case, another approach is the transition state theory (TST) of Gusev et al. (1995).

The simulations of the sorption and diffusion of low molecular weight penetrants on amorphous polymers have covered a range of different polymers with varieties of chemical complexities ranging from flexible polymers with simple chemical structure, like poly(dimethylsiloxane) (PDMS) (Hofmann et al. 2000), poly(isobutylene) (PIB) (Hofmann et al. 2000), polyethylene (PE) (Hofmann et al. 2000), and polypropylene (PP) (Hofmann et al. 2000), to stiff polymers with detailed chemical structure, like polyamides (Heuchel et al. 2004), PIMs (Larsen et al. 2011), TR-PBO (Park et al. 2014) membranes, and on polyelectrolytes (Dobrynin 2004).

The predicted self-diffusion coefficients depend principally on the quality of the force fields used to model the interactions not only between the penetrant and polymer matrix but also by intramolecular interactions between polymer chains. MD simulation of gas diffusion in polymer membranes generates a wealth of information on the mechanism of gas transport but its use is limited to high free-volume rubber matrices and small gas molecules due to prohibitive CPU times for diffusion coefficients smaller than $10^{-8} \text{ cm}^2 \text{ s}^{-1}$. For this reason, today, the technique is not adequate for systematic screening of a large number of polymer candidates and generating data to be used in a materials design approach.

The slowness of MD is an obstacle to the study of polymer properties, but not a barrier. This is especially true when the properties of interest are localized, as in the case of glass transition or diffusivity of small molecules through a polymer matrix. At the far end of what can be achieved, MD can also be applied to study polymer dynamics on the time and length scales of polymer entanglement. For current applications, we focus on methods that have been illustrated with several polymers and are on the verge of being competitive with existing empirical methods.

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Molecular Recognition

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Molecular recognition is a biological phenomenon which realizes special recognition at molecular level in living and chemical systems. The origin of the process lies in the intrinsic capacity of biomolecules to distinguish between other

compounds and interact with them on the base of their molecular complementarities.

The concept of molecular recognition was introduced by the Nobel Prize Emil Fischer who proposed the “lock and key” model to explain the high specificity of an enzyme for its substrate. According to this model, the enzyme and the substrate possess exactly complementary geometric shape that allows them to perfectly join the one with the other (Fisher 1894). Also for the enzyme-substrate interaction, molecular recognition is also the core of other important biological activities such as antigen-antibody binding and DNA duplication and transcription.

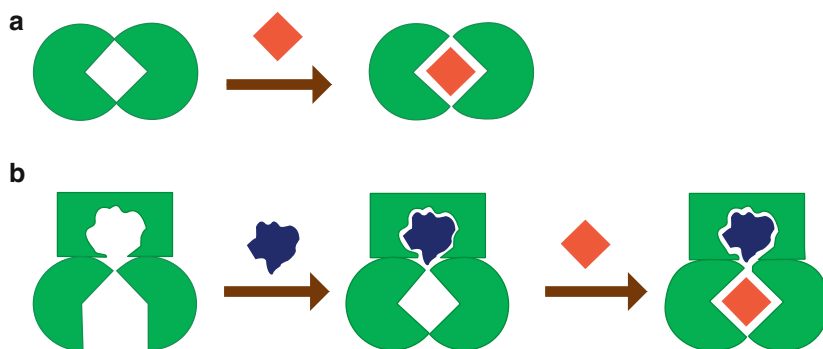
The process is characterized by the onset of specific non-covalent bonding between the interacting molecules. A more modern proposed recognition mechanism called “induced fit” postulated that interacting molecules are flexible and during the recognition process changes of their tri-dimensional structure can be mutually induced (Bosshard 2001). The mutually induced fit mechanism was experimentally proved for many protein-ligand interactions (Wang et al. 2013).

The different postulated recognition mechanisms allow to distinguish static and dynamic molecular recognition. The static recognition, based on the lock and key model, is established between a single guest molecule and a single host binding site. “The dynamic molecular recognition,” which reflects the “induced” fit model, implies the presence of at least two guest molecules. The interaction of the first guest with the first binding site determines conformational change which promotes the binding of the second guest to the second binding site.

A schematic representation of static and dynamic molecular recognition is reported in Fig. 1.

The most important factors driving the molecular recognition are the shape of the interacting molecules, van der Waals attraction forces between them, hydrogen bonding, hydrophobic forces, and electrostatic and electromagnetic effects.

Molecular recognition phenomenon occurring in biological systems inspired numerous studies in



Molecular Recognition, Fig. 1 Static (a) and dynamic (b) molecular recognition

organic chemistry allowing the development of man-made biomimetic recognition materials.

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Molecular Weight Cutoff

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Synonyms

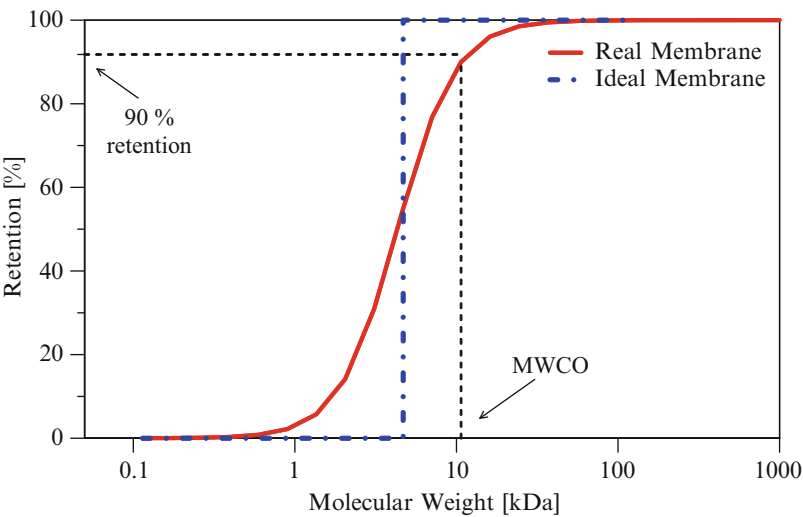
Nominal molecular weight cutoff (NMWCO)

Molecular weight cutoff (MWCO) or nominal molecular weight cutoff (NMWCO) is defined as the minimum molecular weight of a solute that is 90 % retained by the membrane (Drioli and Giorno 2010). MWCO or NMWCO is determined by evaluating the retention of the membrane for components of different molecular weights as plotted in Fig. 1 (Strathmann et al. 2006). The cutoff curve should be as sharp as possible for practical applications (Strathmann et al. 2006).

Test conditions, such as applied pressure, concentration, temperature, etc., influence greatly the results, but no standardized experimental method is currently available. However, it is recommended to use a transmembrane pressure of 100 kPa, a feed concentration of 0.1 %, and a test temperature of 25 °C and high agitation (Cheryan 1998; Strathmann et al. 2006). Several compounds with different molecular weights are often being used in MWCO determination such as polyethylene glycols, dextran, etc. (Cheryan 1998).

In Table 1, a few examples of commercial UF membranes have been given. An example of MWCO given by the manufacture can be 10 kDa; thus the membrane retains molecules with a molecular weight larger than 10 kDa which could be some proteins. However, for real applications, it will depend on the objective of the filtration process, e.g., separation of proteins from salts, the more challenging protein-protein separation, etc. The final

Molecular Weight Cutoff, Fig. 1 Relationship between retention and molecular weight cutoff of ideal and real membrane (Cheryan 1998)



Molecular Weight Cutoff, Table 1 Some examples of UF commercial membranes with their respective molecular weight cutoff

Manufacture	Type	Material	MWCO [Da]	Application
Koch membrane systems	HFK-328, HFK-131, HpHT™	PES	5,000–10,000	Whey and milk concentration
	HFK, XL-1000™			
Pall	HFM-180	PVDF	100,000	Clarification in dairy industry
	AIP-0013, ACP-0013, AHP-0013, LOV-3010	PAN	6,000, 13,000, 50,000, 80,000	Pharmaceutical applications; purification and processing of aqueous enzymes and protein solutions, raw water pretreatment to pharmaceutical water purification plant
Nitto Denko – hydranautics	HYDRAcap	PES	150,000	Surface water, groundwater, seawater, and wastewater as either primary treatment or as NF/RO pretreatment
Toray	HFU series	PVDF	150,000	Industrial water treatment, seawater desalination for RO pretreatment, wastewater tertiary treatment
MICRODYN-NADIR	NADIR®	PES, PSU, regenerated cellulose PVDF	4,000–150,000, 100,000, 500,000, 150,000	Wide range of applications within food and beverage, pharma and biotech, textile, etc.

selection must be made based on experimental data (Cheryan 1998).

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Molecularly Imprinted Membranes

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Molecularly imprinted membranes (MIMs) are biomimetic materials which have molecular recognition capacity. Thanks to the presence of specific molecular recognition sites in their matrix, these advanced functional membranes are able to discriminate between a molecule of particular interest named “template” and other analytes. The specific recognition is due to the chemical and spatial complementary existing between the template and the recognition sites of the membrane. Molecularly imprinted membranes are identified as a special format of imprinted polymers, and their development is due to the combination of the bioinspired imprinting technique and the oldest membrane science. Exploiting the advantages of both technologies, the development of such systems has made a significant contribution to the improvement of detection and separation processes at the molecular level. In comparison with the traditional application of imprinted polymers, processes based on imprinted membranes are more efficient due to possibility of operate in continuous, without additives, and at low temperature, thus reducing the operating costs. In addition, the specificity of an imprinted membrane is enhanced with respect to a traditional membrane, but in the meantime the separation efficiency is preserved.

Two different transport mechanisms are known: *facilitated permeation* and *retarded permeation*. In the first case, the transport of the template through the membrane is more rapid than the transport of other compounds. The reason of this behavior is due to the presence of a preferential pathway for the template in the membrane which is formed via binding to and dissociating from neighbored recognition sites, thus facilitating its permeation. On the contrary, other solutes are subjected to the slow nonspecific transport. The second transport mechanism is characterized by a retarded permeation of

the template through the membrane, owing to the affinity binding with the recognition sites distributed in the membrane matrix.

The most commonly developed molecularly imprinted membranes have flat-sheet configuration and are prepared via the phase inversion technique from a viscous solution of the membrane-forming polymer which contains also template molecules. The molecular memory of the template is induced in the membrane at the same time as the membrane is forming from its polymer solution. Membranes having hollow-fiber configuration are also prepared using the same technique. Thanks to their high specificity, MIMs are useful for molecular recognition of a variety of substances in food, environmental, and pharmaceutical fields. Most relevant applications are enantiomeric separations (Noaman and Park 2008), purification of drugs (Trotta et al. 2007), enrichment of food additives (Donato et al. 2010), decontamination of water (Sergeyeva et al. 2008), and many others. Imprinted membranes having catalytic properties (Kalim et al. 2005) or useful for specific recognition in organic environment (Del Blanco et al. 2012) also attract the attention of the scientists.

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Monitoring NOM-Based Fouling

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Definition

Monitoring of NOM or natural organic matter-based membrane fouling refers to identifying exclusively the NOM components that contribute to membrane fouling in drinking water production. This may be of interest for various reasons including to better understand from a fundamental perspective what contributes to fouling, to implement strategies to mitigate fouling, or to control and optimize the filtration processes.

Overview

The objective of monitoring NOM-based membrane fouling will impact the method of choice for monitoring. A variety of water matrix characterization techniques exist that have as their basis the experimental analysis of NOM, and which may require fractionation of the NOM into its various components prior to some form of detection. NOM constituents can be characterized based on their hydrophobicity and their molecular weight. Among the techniques that involve separation is liquid chromatography/organic carbon detection (LC-OCD), which most commonly involves the use of size exclusion chromatography or SEC. In order to obtain information on the structural and functional characteristics without separation, more sophisticated analytical approaches may be required that rely on different spectroscopic approaches. This may include nuclear magnetic resonance (NMR), infrared spectroscopy (IR), Fourier transform infrared spectroscopy (FTIR), or fluorescence excitation-emission matrices (FEEM). A comprehensive review of the methods that can be used for characterization of NOM will be found in the review by Matilainen et al. (2011). When the objective is to control the fouling

process, it is advantageous to have on-line approaches that provide real-time updates. This is normally not feasible with techniques that rely on separation of the components for analysis. Among techniques that can be employed in this manner are the spectroscopic-based approaches.

Cross-References

- [Fouling In Membranes](#)
- [Irreversible Fouling](#)
- [Membrane Fouling](#)

References

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Monolithic Membranes

Jordi Llorca

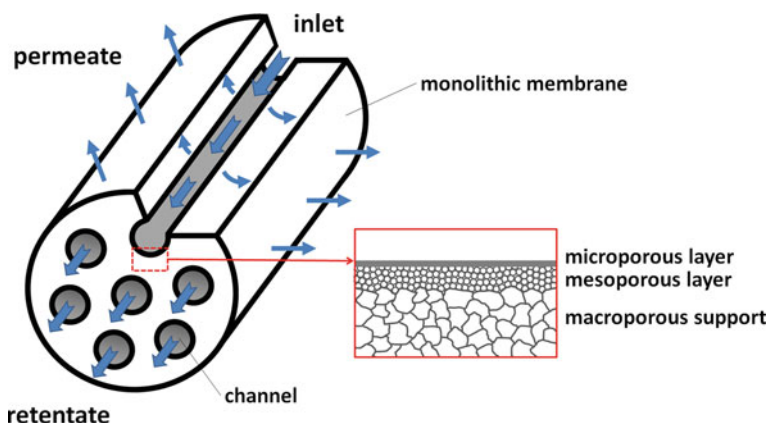
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Synonyms

[Honeycomb membrane](#); [Structured membrane](#)

Membranes are usually configured in three ways: (i) as long cylinders such as hollow fibers, capillaries, or tubes, (ii) as sheets which are either rolled up or maintained in a flat condition, and (iii) as various monolithic designs with a plurality of cylindrical, flower-like, or honeycomb-like channels (Fig. 1). Channels can vary in diameter and can be present in multiple numbers. Each channel is coated with a membrane layer.

The body of most monolithic membranes is made up of ceramic inorganic materials with macropores (>50 nm), such as alumina, zirconia, titania, or silicon carbide, supporting a multilayer



Monolithic Membranes, Fig. 1 Drawing of an element of a ceramic monolithic membrane. Channels are coated with a membrane layer, which is usually constituted by a first macroporous layer strongly anchored to the ceramic

body, a second mesoporous layer that acts as binder and a third microporous layer, which mainly determines the separation characteristics of the membrane

porous structure exhibiting a non-deformable porosity (Hsieh 1991). Usually, each channel is coated with a membrane layer comprising a first macroporous layer disposed directly on the surface of each channel, a second mesoporous intermediate layer disposed on the first macroporous layer, and a third microporous layer (micropores < 2 nm) disposed on the second mesoporous intermediate layer. The membrane layers are normally sintered in place, making an extremely strong ceramic-to-ceramic bond with the monolithic membrane body. Synthetic and modified natural polymeric materials are also being used and, more recently, monolithic membranes containing carbon fibers with great mechanical strength (enabling to withstand working pressures greater than 50 bars).

Ceramic monolithic membranes offer significant advantages over other types of membranes in many applications operating under extreme conditions because of their intrinsic properties, i.e., rigid porous structure, high-temperature resistance, high-chemical resistance to aggressive aqueous and organic media, and insensitiveness to biological attack. These applications typically are the treatment of waste liquids and gases, liquid processing including drinking water and separation of biomolecules, and product recovery in industry.

For liquid filtration, existing monolith membranes use a cross-flow filtration configuration in

which a single feed stream that enters the filtration channels of a ceramic membrane element is divided into a permeate (solution that passes through the membrane and exits transverse to the monolith flow path) and a retentate (solution that is retained by the membrane and exits parallel to the monolith flow path and is recycled back into the feed stream). The separation is driven by the pressure difference from one side of the membrane to the other, commonly referred to as transmembrane pressure. The parallel flow of the feed stream, combined with the boundary layer turbulence created by the cross-flow velocity, continually sweeps away particles and other substances that would otherwise build up on the membrane surface (Lee 2011). For gas separation, it is often advantageous to use two discrete feed streams in which one of the feed streams is a sweep gas to keep permeate concentration low to maximize the driving force for separation. This requires two discrete flow paths in fluid communication only through the porous walls of the monolith structure.

According to the application, the membrane elements can be also tailored with appropriate active surfaces, such as catalysts, resulting in the so-called catalytic monolithic membranes. They have been used in industry for a variety of coupling reactions (hydrogenation, dimerization, etc.), although their drawback is the small catalytic surface area per unit volume of the reactor.

Cross-References

► [Monolithic Reactor](#)

References

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Monolithic Reactor

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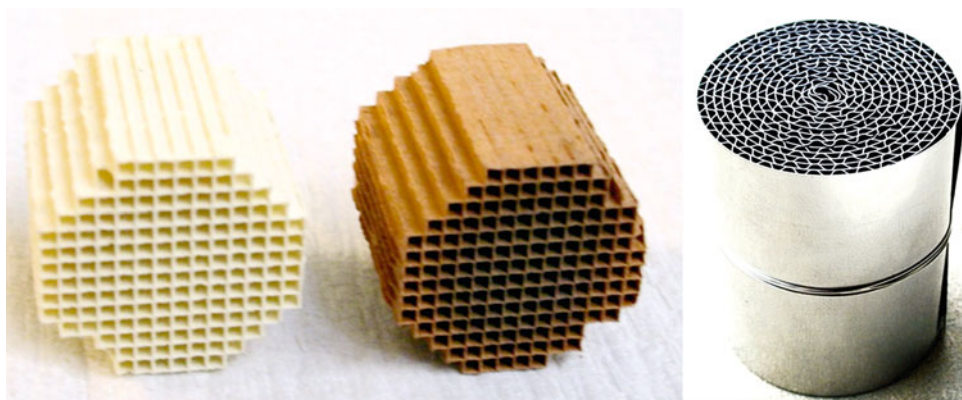
Synonyms

[Structured reactor](#)

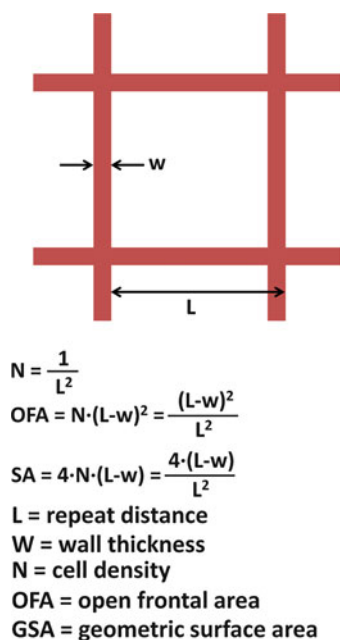
Monoliths are structures that contain various types of interconnected or separated channels (straight, wavy, or crimped) in a single block of material (e.g., honeycombs, foams, or interconnected fibers). Most monolith reactors consist of one piece of ceramic material. This ceramic block contains a large number of parallel channels extending over the entire length of the

block, separated by thin walls. The channels normally have circular, square, or triangular cross sections but also channel geometries produced by wrapping up flat metal sheets with corrugated metal sheets in between (Fig. 1). Monolithic reactors are those filled with monoliths that are either made of porous catalytic material or the catalytic material is deposited (washcoated) in the channels of an inert monolithic support (Avila 2005). In both arrangements, the channel walls function as catalyst and the channels provide space for flow of gas and/or liquid. Another type of monolithic reactors are those where the thin walls act directly as membranes or are used as a substrate for depositing materials that serve as membranes for separation and/or purification purposes.

Currently, ceramic and metallic monoliths are the two major types of monolith supports used. Ceramic monoliths are mostly prepared by extrusion while metallic monoliths are normally made by corrugation. The ceramic material cordierite (magnesium aluminum silicate) is commonly used because it is cheap, it can be easily manufactured with high porosity, and it has a very small thermal expansion coefficient (Cybulski 1998). Channel size and shape affect the pressure drop across the channel and the hydrodynamics of the fluid phases. The monolith themselves have a square, oval, racetrack, or round geometry, depending on the application. Larger volumes of monolith structures are obtained by stacking smaller building blocks.



Monolithic Reactor, Fig. 1 400 cpsi cordierite monolith before (*left*) and after (*middle*) catalyst deposition and 1200 cpsi metallic monolith (*right*)



Monolithic Reactor, Fig. 2 Transversal section of a square-channel monolith with the parameters employed to characterize the monolith geometry

Different types of distributors can be used to achieve the desired uniform flow distribution over the monolith cross section, such as spray nozzles, shower heads, hole plates, glass frits, and static mixers.

In the case of the square-channel monoliths, the monolith geometry is fully defined by two parameters: the channel size or repeat distance (L), and either the wall thickness (w , usually between 0.06 and 0.5 mm) or cell density (N), which is defined as number of cells per square inch (cpsi) and typically ranges between 100 and 1200 (Fig. 2). Other parameters commonly used to characterize the monolith structure are the void fraction, which varies between 0.5 and 0.9 and is frequently expressed as the open frontal area (OPA), the geometric surface area (GSA), and the surface-to-volume ratio (Williams 2001).

Monolithic reactors have some common features in most of the applications for which they are used. Compared with other types of reactors commonly used in industry they have numerous advantages, such as low pressure drop, especially under high fluid throughputs; high specific

external surface area for mass transfer; elimination of internal diffusion limitations when thin walls are used; low axial dispersion and back-mixing, and therefore high product selectivity; reduction of fouling and plugging, and thus extended lifetime; and as a result of the application of a regular structure, the scale-up to industrial relevant size is considerably easier. The main disadvantages are potential low radial heat transfer rate, and thus difficulty in temperature control, especially for ceramic monolith supports.

Monolith reactors were developed for the cleaning of exhaust gases from combustion processes, both in cars and large power plants. For these processes, monolith reactors offer an irresistible combination of low pressure drop and high surface area. Due to their significant advantages over conventional types of reactors, monoliths have also applications in gas phase, gas-liquid phase, liquid phase, or gas-liquid-solid phase reactions in the environmental and chemical, petrochemical, biochemical, and energy industries.

Cross-References

► [Monolithic Membranes](#)

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Monovalent Cation Selective Ion-Exchange Membranes

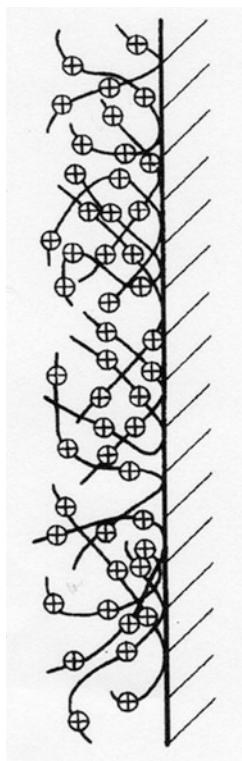
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Monovalent cation selective ion-exchange membranes are developed by forming the polycation

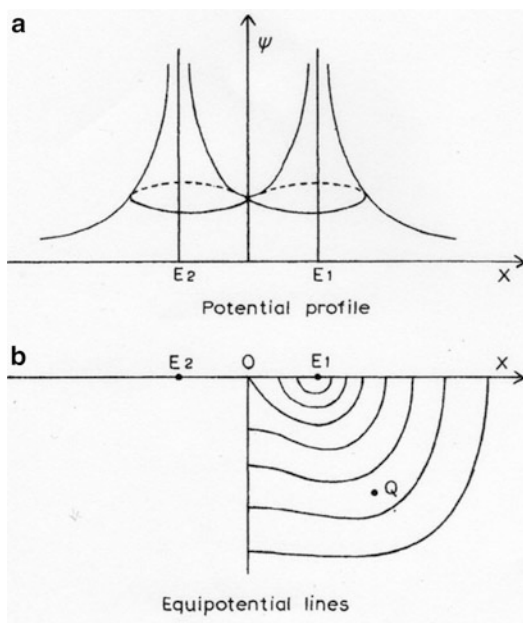
Monovalent Cation Selective Ion-Exchange Membranes,

Fig. 1 Polycation layer formed on the cation-exchange membrane. Tanaka and Seno (1981), Fig. 8



layer on the surface of the cation-exchange membrane as illustrated in Fig. 1 for preventing CaSO_4 precipitation in electrodialytic seawater concentration. In the polycation layer, positively charged groups pack closely together, and Coulomb and Born repulsive force exert on surrounding cations. The potential produced by two adjacent polycation groups is illustrated in Fig. 2; under the influence of an electric field, a mobile cation Q moves across the lowest potential barrier between two polycation groups E_1 and E_2 . Any mobile cation must pass over the potential barrier of the polycation layer in order to permeate the membrane. Under these circumstances, the transport of divalent ions across the membrane becomes more difficult than for monovalent ions, because greater energy is required for doubly charged cations to pass over the barrier.

The mechanism of monovalent cation permselectivity increase (divalent ion permeability decrease) is discussed by applying the Boltzmann equation to the potential profile illustrated in Fig. 3 (Tanaka and Seno 1981). In this system, the feed solution contains monovalent



Monovalent Cation Selective Ion-Exchange Membranes, Fig. 2 Potential distribution in the polycation layer. Tanaka and Seno (1981), Fig. 9

cation A and divalent cation B with common anions.

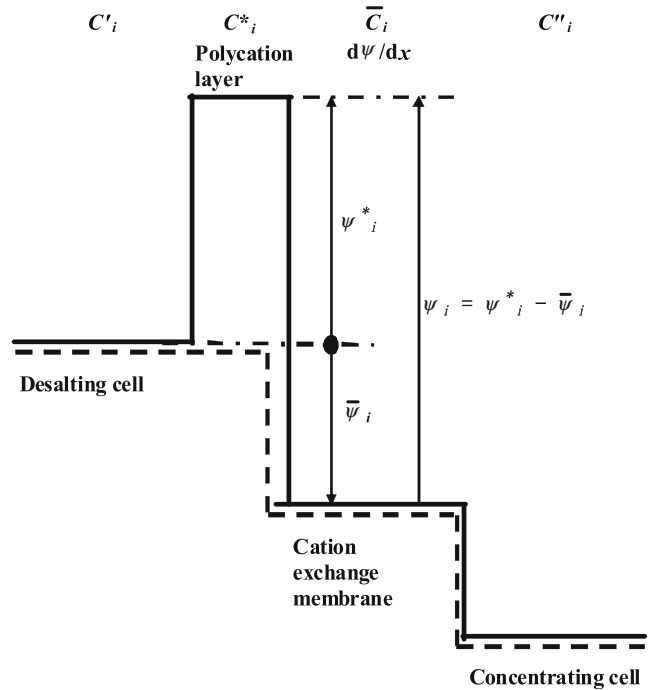
When no polycation layer is formed on the membrane surface, the potential profile is depicted schematically by the dotted line in Fig. 3. Under an applied electric current, the concentration polarization is assumed to be neglected because the boundary layer is diminished due to forced flowing solutions in desalting cells. Thus, the relationship between the ion concentration in the desalted solution and in the membrane is approximately expressed as follows, applying the Boltzmann equation and taking the potential height in the desalted solution phase as standard:

$$\begin{aligned}\bar{C}_A &= C'_A \exp\left(-\frac{\bar{\psi}_A}{RT}\right) \\ \bar{C}_B &= C'_B \exp\left(-\frac{\bar{\psi}_B}{RT}\right)\end{aligned}\quad (1)$$

where $\bar{C}_i$ and C'_i are the concentration of ion i in the membrane and in the desalted solution, respectively. $\bar{\psi}_i$ is the potential height in the membrane for ion i measured from the desalted solution

Monovalent Cation Selective Ion-Exchange Membranes,

Fig. 3 Potential profile across a polycation layer and a cation-exchange membrane. Dotted line shows the profile with no polycation layer. Tanaka and Seno (1981), Fig. 10



phase. The ion fluxes are introduced from Eq. 1 and the potential gradient term in the Nernst-Planck equation as

$$\begin{aligned} J_A^0 &= -z_A \bar{u}_A \bar{C}_A \frac{d\varphi}{dx} = -z_A \bar{u}_A C'_A \frac{d\varphi}{dx} \exp\left(-\frac{\bar{\psi}_A}{RT}\right) \\ J_B^0 &= -z_B \bar{u}_B \bar{C}_B \frac{d\varphi}{dx} = -z_B \bar{u}_B C'_B \frac{d\varphi}{dx} \exp\left(-\frac{\bar{\psi}_B}{RT}\right) \end{aligned} \quad (2)$$

where J_i^0 , z_i , and u_i are the flux, the valence, and the mobility of ion i . $d\varphi/dx$ is the potential gradient in the membrane. The permselectivity coefficient of ion B against ion A; $(T_A^B)^0$ is expressed using Eq. 2 as follows:

$$\begin{aligned} (T_A^B)^0 &= \frac{\left(\frac{z_B J_B^0}{z_A J_A^0}\right)}{\left(\frac{z_B C'_B}{z_A C'_A}\right)} \\ &= \frac{z_B \bar{u}_B}{z_A \bar{u}_A} \exp\left(-\frac{\bar{\psi}_B - \bar{\psi}_A}{RT}\right) \end{aligned} \quad (3)$$

When the polycation layer is formed on the membrane surface, the potential profile is formed

as indicated by the continuous line in Fig. 3. Concentration of ion i in the polycation layer is expressed by

$$\begin{aligned} C_A^* &= C'_A \exp\left(-\frac{\psi_A^*}{RT}\right) \\ C_B^* &= C'_B \exp\left(-\frac{\psi_B^*}{RT}\right) \end{aligned} \quad (4)$$

where C_i^* and ψ_i^* are, respectively, the concentration and the potential height in the polycation layer for ion i .

When the ionic mobility in the membrane phase is rather high, ion concentration in the membrane is primarily controlled by the ratio of uptake of those ions from the solution phase. This situation is observed for the carrier-mediated transport of ions through liquid membranes (Bloch 1970). Since the polycation layer serves as a barrier to ionic transport across the membrane system, and the permeation step through this barrier is rate determining, it is reasonable to suppose that a kinetic-controlled mechanism holds in the present case. Under these conditions, it is

safely considered that the concentration ratio in the membrane, $\bar{C}_A/\bar{C}_B$, is primarily determined by the concentration ratio in the polycation layer, C_A^*/C_B^* . If $\bar{C}_i$ is tentatively assumed to be proportional to C_i^* , then the ion fluxes across the membrane will be given by Eq. 5:

$$\begin{aligned} J_A^0 &= k z_A \bar{u}_A C_A' \frac{d\varphi}{dx} \exp\left(-\frac{\psi_A^*}{RT}\right) \\ &= k J_A^0 \exp\left(-\frac{\psi_A^* - \bar{\psi}_A}{RT}\right) J_B^0 \\ &= k z_B \bar{u}_B C_B' \frac{d\varphi}{dx} \exp\left(-\frac{\psi_B^*}{RT}\right) \\ &= k J_A^0 \exp\left(-\frac{\psi_B^* - \bar{\psi}_B}{RT}\right) \end{aligned} \quad (5)$$

k is the constant. T_A^B is derived from Eq. 5 as follows:

$$\begin{aligned} T_A^B &= \left(\frac{z_B J_A}{z_A J_B}\right) \left(\frac{z_A C_A'}{z_B C_B'}\right) \\ &= \frac{z_B \bar{u}_B}{z_A \bar{u}_A} \exp\left(-\frac{\psi_B^* - \psi_A^*}{RT}\right) \\ &= (T_A^B)^0 \exp\left(-\frac{\psi_B - \psi_A}{RT}\right) \end{aligned} \quad (6)$$

The potential $\psi_i = \psi_i^* - \bar{\psi}_i$ is that of polycation layer relative to that in the membrane phase. The potential difference $\psi_B - \psi_A$ provides a mechanism for the separation of ion A from ion B and can be estimated from the electrodialysis experiment as follows:

$$\begin{aligned} \psi_B - \psi_A &= RT \ln \left[\left(\frac{J_B^0}{J_A^0} \right) / \left(\frac{J_B}{J_A} \right) \right] \\ &= RT \ln \left[(T_A^B)^0 / T_A^B \right] \end{aligned} \quad (7)$$

Monovalent Cation Selective Ion-Exchange Membranes, Table 1 Specifications of the electrodialyzer

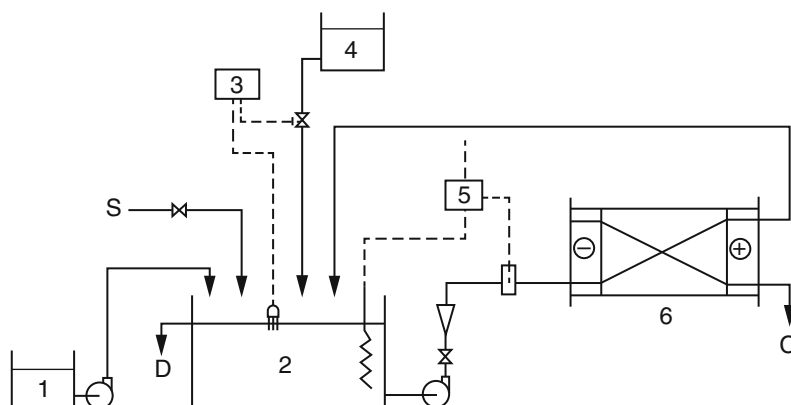
Membrane area	5 dm ² (50 cm height, 10 cm width)
Space between membranes	0.75 mm
Number of desalting cells	21
Number of concentrating cells	20
Membrane	Selemion CMV-4/ASV-4
Spacer	Diagonal net
Cathode	Iron
Anode	Graphite

Tanaka (1974), Table 1

Specifications of the electrodialyzer are shown in Table 1. The flow sheet of the test apparatus is illustrated in Fig. 4 (Tanaka 1974). Seawater was supplied into each desalting cell at linear velocity of 5 cm/s through a circulation tank, keeping the temperature to 25 °C and applying current density of 4 A/dm². When the salt concentration of the concentrated solution reached a stationary value, polycations (Nonisold, Daiichi Kogyo Pharmaceutical Co. Ltd.) were supplied continuously from the reservoir into the circulation tank to keep its concentration at a constant value. During the electrodialysis, the concentrated solutions

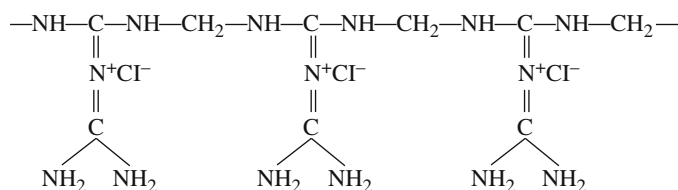
Monovalent Cation Selective Ion-Exchange Membranes, Fig. 4 Flow sheet of the test apparatus.

(1) Reservoir of the polycation solution. (2) Circulation tank. (3) pH controller. (4) Reservoir of HCl. (5) Thermoregulator. (6) Electrodialyzer. S seawater, D desalted solution, C concentrated solution. Tanaka (1974), Fig. 1

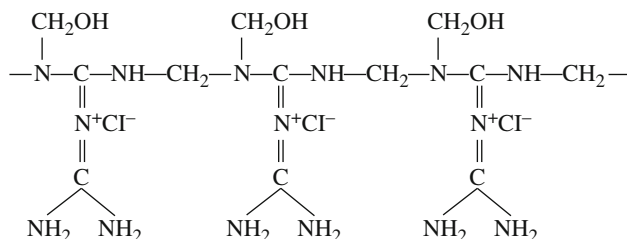


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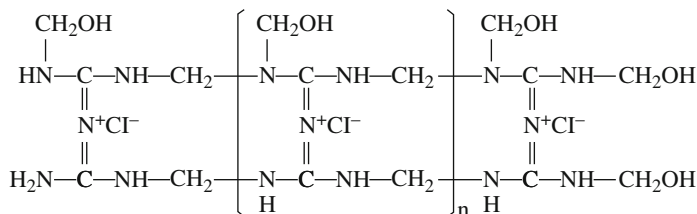
Fig. 5 Dicyandiamide-
formaldehyde condensate.
Tanaka and Seno (1981),
Fig. 3



(I)



(II)



(III)

Monovalent Cation Selective Ion-Exchange Membranes, Table 2 Elementary analysis of Nonisold (wt. %)

Element	Observed value	Calculated value		
		Structure I	Structure II	Structure III
C	27.10	24.09	26.75	31.34
H	5.05	5.39	5.61	5.26
N	38.00	46.82	38.99	36.55
O			8.91	8.35
Cl		23.70	19.74	18.50

Tanaka and Seno (1981), Table 3

were analyzed at regular intervals and the fluxes of Na^+ , Mg^{2+} , and Ca^{2+} were calculated. Prior to the next experiment, the polycations fixed on the membrane surfaces were completely removed by feeding acidified seawater into desalting cells.

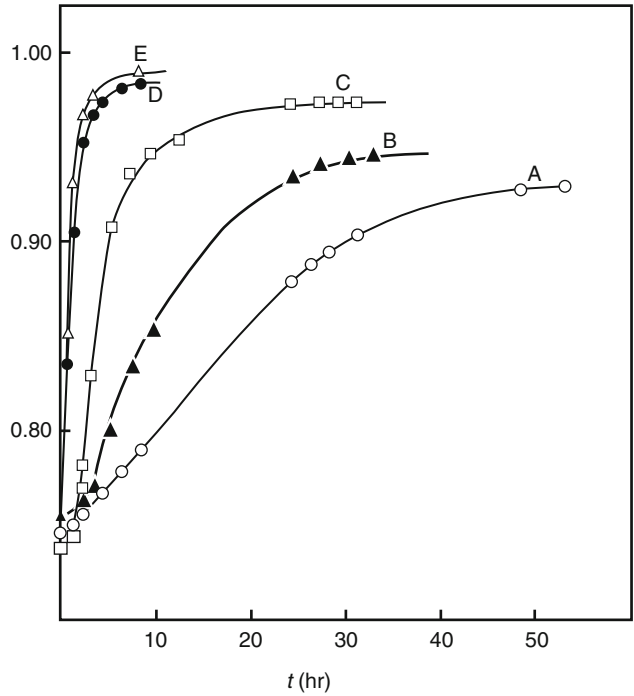
The polycations Nonisold is a condensate of dicyandiamide and formaldehyde. The suggested chemical structures of which are shown in Fig. 5. Results of C, H, and N analysis

by a Yanagimoto CHN Corder MT-2 are listed in Table 2.

Figure 6 shows the changes of monovalent ion concentration ratio $\varepsilon = (C_{\text{Na}} + C_K) / (C_{\text{Na}} + C_K + C_{\text{Mg}} + C_{\text{Ca}})$ with time. Figure 7 shows ε versus cell voltage V_{cell} and energy consumption E . V_{cell} and E are extremely increased when ε is increased beyond 0.99. This phenomenon is caused by salt concentration decrease at the interface between the polycation layer and the cation-exchange

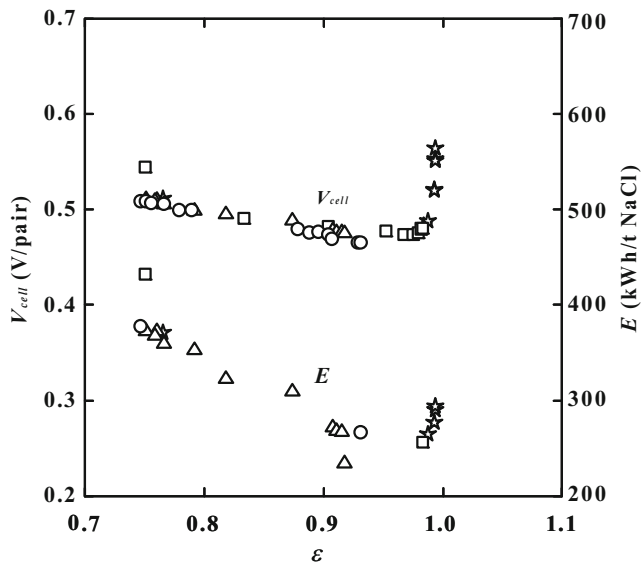
**Monovalent Cation
Selective Ion-Exchange
Membranes,**

Fig. 6 Changes of monovalent ion ratio in concentrate ε with time. Polycation concentration: 0.049 (A), 0.092 (B), 0.508 (C), 0.987 (D), 2.074 (E) mg/dm^3 . Tanaka (1974), Fig. 3



**Monovalent Cation
Selective Ion-Exchange
Membranes,**

Fig. 7 Monovalent ion ratio in concentrate ε versus cell voltage and energy consumption. Polycation concentration: 0.049 ($\circ$), 0.092 (Δ), 0.987 ($\square$), 2.074 ($\star$) mg/dm^3



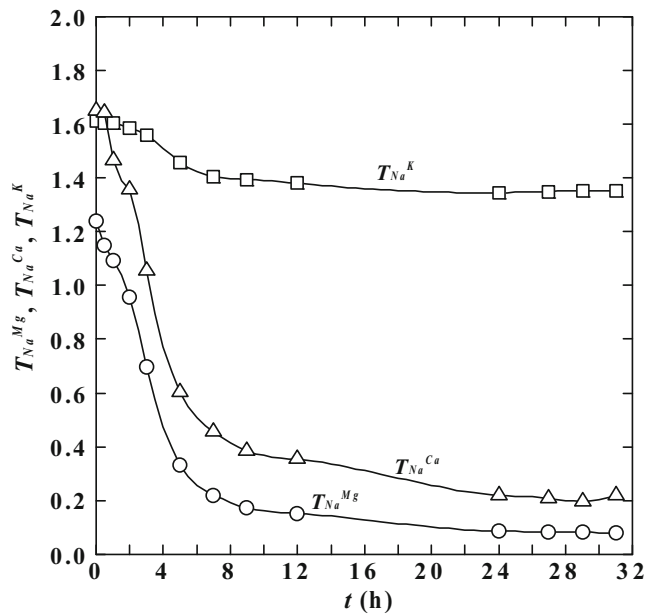
membrane due to the bipolar type structure formation.

Figure 8 shows an example of T_A^B changes with time in the above electrodialysis experiment. Figure 9 is potential difference $\psi_B - \psi_A$ calculated from Fig. 8 using Eq. 7. The

potential difference for transporting divalent cations (Mg^{2+} and Ca^{2+}) is drastically increased comparing to the values for monovalent cations (K^+). This phenomenon gives the monovalent cation selectivity to the cation-exchange membrane.

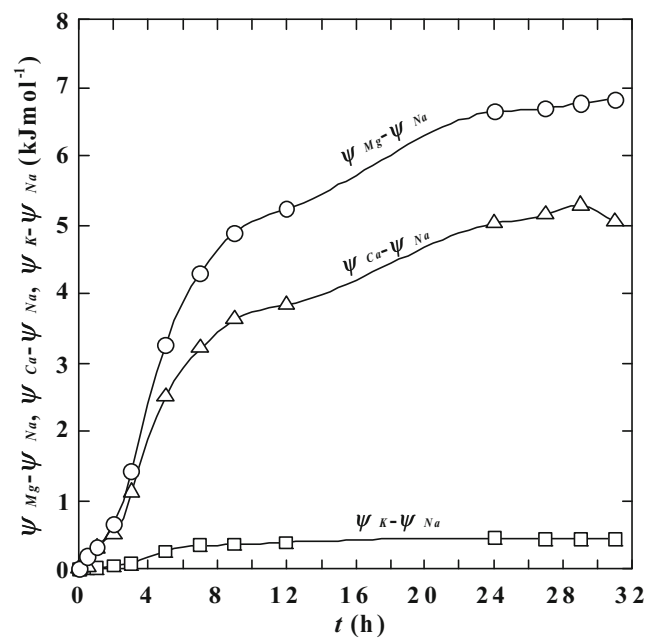
**Monovalent Cation
Selective Ion-Exchange
Membranes,**

Fig. 8 Changes of T_A^B with time. Polycation concentration: 0.508 mg/dm^3



**Monovalent Cation
Selective Ion-Exchange
Membranes,**

Fig. 9 Changes of $\psi_B - \psi_A$ with time. Polycation concentration: 0.508 mg/dm^3 . Tanaka and Seno (1981), Fig. 11



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MOR Membrane

► [Mordenite Membrane](#)

Mordenite Membrane

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Synonyms

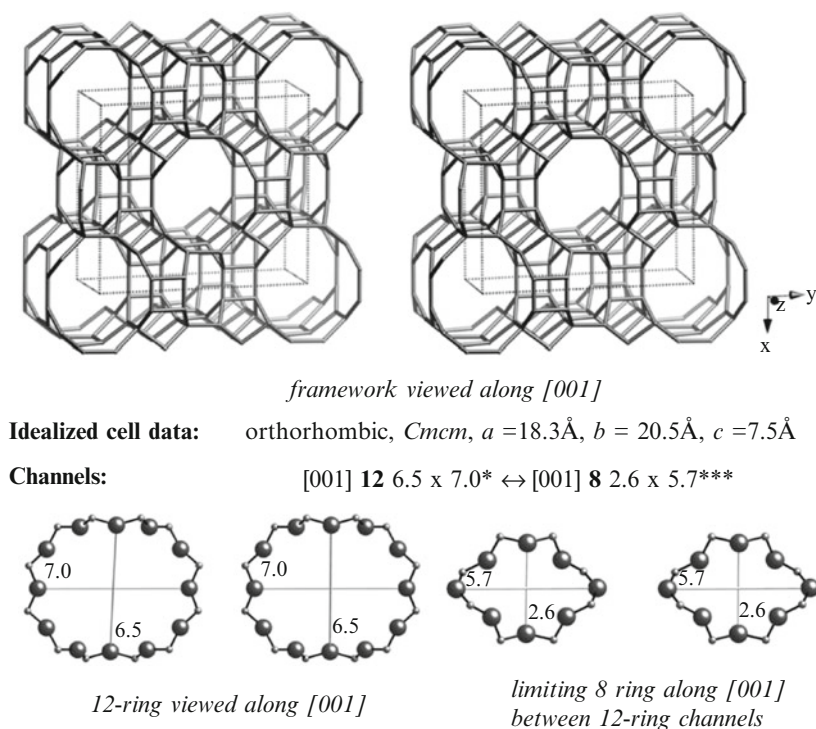
MOR membrane

Mordenite (MOR) is a high-silica zeolite, with a molecular formula $\text{Na}_8(\text{H}_2\text{O})_{24}[\text{Al}_8\text{Si}_{40}\text{O}_{96}]$, in which the Si, Al content of the framework and the cation content of the cavities are moderately variable. The Si/Al ratio could be varied between 4 and 20. MOR-type zeolite consists of 12-Membered Ring (MR = straight channels ($6.5 \times 7.0 \text{ \AA}$) parallel to the c-axis, interconnected to tortuous 8-MR

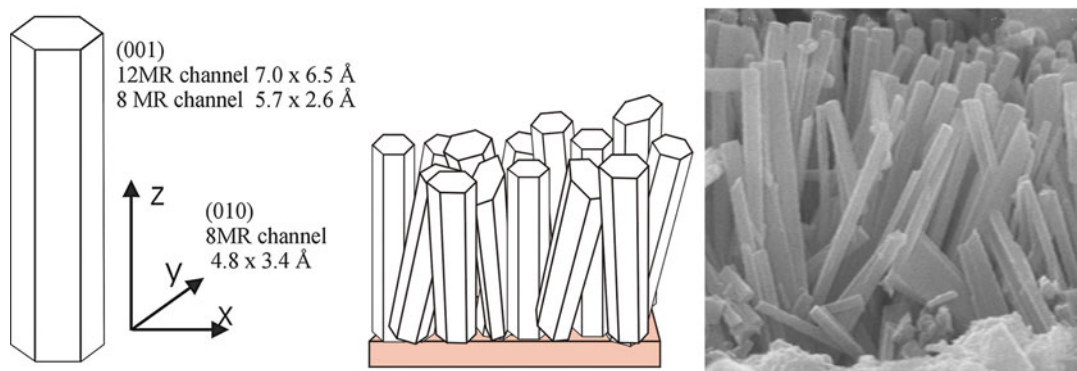
channels ($2.6 \times 5.7 \text{ \AA}$) in the a-axis, see Fig. 1, (International Zeolite Association commission). Typical morphology of the crystals corresponds to long needles that run along the c axis (see Fig. 2), but other morphologies could be also observed.

Mordenite membranes have been prepared by different methods: the vapor phase transport method, direct (unseeded) hydrothermal synthesis with or without template, and see [Seeded Hydrothermal Synthesis for Zeolite Preparation](#). This last method could be considered as the most convenient in terms of synthesis time reproducibility and is easy to scale up.

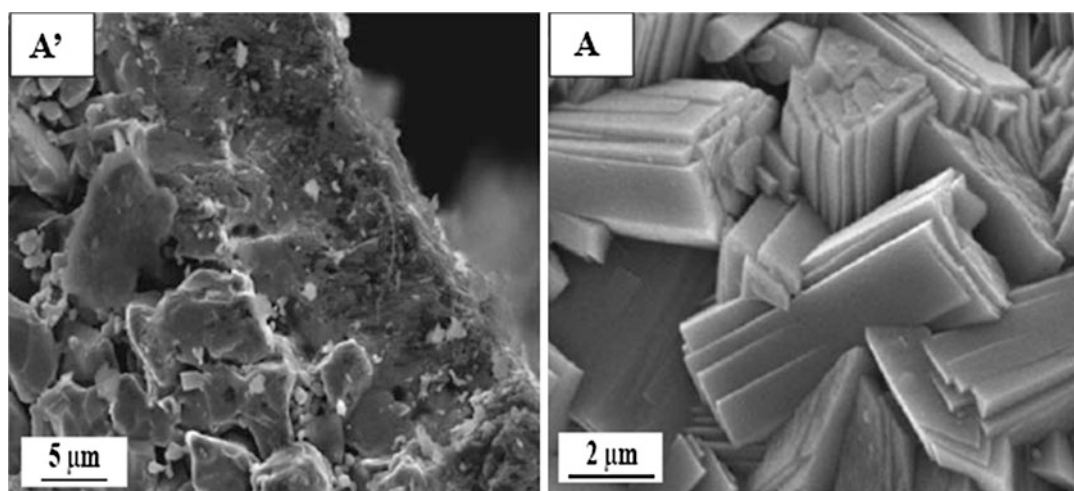
The orientation of the zeolite mordenite crystals in the MOR membranes is very important, favoring the transport of the molecules through the big 12MR channels, see Fig. 2. Control of the orientation could be achieved by secondary growth and control of the synthesis gel composition (Li et al. 2003). Figure 3 shows random orientation of zeolite crystals in mordenite membranes, (Navajas et al. 2007).



Mordenite Membrane, Fig. 1 Framework topology of MOR and pore size of the channels. IZA structure commission



Mordenite Membrane, Fig. 2 Mordenite crystal orientation on a cordierite monolithic structure (Reprinted with permission from Ulla et al. (2004) *Chem. Commun* 528–529)



Mordenite Membrane, Fig. 3 Top view and cross section of mordenite membranes prepared by secondary growth method (Reprinted with permission from Navajas et al (2007) *J Membr. Sci.* 299 (1–2), 166–173)

Due to the relatively big pore size 0.65 nm these membranes have not been tested in separation of small molecules of permanent gases, instead these membranes have been proposed as good candidates in pervaporation separation, (see [Mordenite Membrane in Pervaporation](#)). In particular, due to the relatively high silica to aluminum ration these zeolites are selected for water pervaporation in acidic mixtures, (see [Acetic Acid Dehydration by Pervaporation Zeolite Membranes](#)).

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Mordenite Membrane in Pervaporation

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Mordenite membranes belong to the inorganic microporous (pores below 2 nm according to IUPAC definition) membrane group. These membranes are applied in gas separation and pervaporation. In the case of mordenite, since the kinetic diameter of most of the permanent gases is bigger than the pore size of this structure 0.7 nm (see entry “► [Mordenite Membrane](#)”), the membranes are not applied in gas separation, and pervaporation is the main application envisioned in the literature. Furthermore the relatively high Si/Al ratio and moderate hydrophilicity make these membranes perfect candidates for dehydration of acidic mixtures by pervaporation (see entry “► [Acetic Acid Dehydration by Pervaporation Zeolite Membranes](#)”).

There are many reported data for pervaporation of water/alcohol mixtures; the performance is lower compared to the more hydrophilic zeolite A membranes (Arruebo et al. 2008). In the separation of a mixture of H₂O/isopropanol, 10% wt/90%wt at 75 °C water fluxes are in the order of 0.1–0.2 kg/hm² in the case of MOR, and in the case of H₂O/isopropanol 10%wt/90%wt at same temperature, values of 2–9 kg/hm² could be found. Thus, the main application of mordenite membranes in pervaporation is in the case of dehydration of acidic mixtures where zeolite A membranes degrade, while MOR membranes remain stable. The economic feasibility of mordenite membranes for pervaporation of acetic acid/water mixtures has been also studied by the researchers of Mitsubishi (Sato et al. 2011). The membrane performance in pervaporation was measured in a feed mixture of water (50 wt%)/AAc (50 wt%) to be 10.9 kg m²/h for permeate flux and to be 0.77×10^{-6} mol m²/sPa for water permeance with separation factor of 500 at 130 °C.

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Mosaic Membranes

Karel Friess

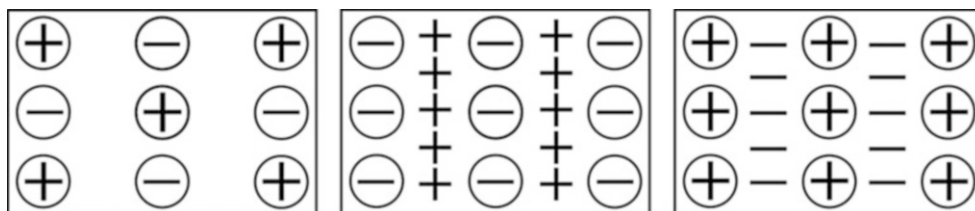
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Synonyms

[Charged mosaic membrane](#); [Ion-exchange mosaic membranes](#)

Mosaic membranes (MM) are composed of macroscopic fixed domains of cation exchange (negatively charged) and anion exchange (positively charged) arranged in parallel resins separated by a neutral polymer or ion-exchange channel matrix (see Fig. 1) (Soellner 1932; Strathmann 2004; Wu et al. 2006). Inside channels with positive charge is higher concentration of negatively charged anions and vice versa. MM are effective in concentrating of diluted electrolytes in the presence of hydrostatic pressure and chemical potential gradient (*piezodialysis*) (Sata 2004). Mosaic membrane can be used also for separation of electrolytes from nonelectrolytes.

MM can be prepared (Sata 2004) by various methods: (i) cross-linking reaction of two different copolymers with ion-exchange resins; (ii) cutting a laminated block of alternating cation-/anion-exchange membranes into films (perpendicular to the membrane surface); (iii) casting (layer-by-layer) a block-copolymer film with one exchange groups, insulating layer, and



Mosaic Membranes, Fig. 1 Schematic draw of structure of mosaic membrane configurations: cation- and anion-exchange domains in neutral matrix (*left*), cation-exchange

domains in anion-exchange matrix (*middle*), and anion-exchange domains in cation-exchange matrix (*right*)

block-copolymer film with opposite exchange groups; (iv) casting of a film using a dispersion containing ion-exchange microsphere gels and polymer.

Alternative approaches of preparation of MM consist in ion-exchange asymmetric membrane with a uniform distribution of counterion-exchange particles in the dense integral skin layer (Linder and Kedem 2001) or in use of hybrid materials containing both positive and negative charges (Liu et al. 2005).

Cross-References

► Ion-Exchange Membranes

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Multi-effect Membrane Distillation

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Multi-effect membrane distillation (MEMD) is a promising technology that can avoid the disadvantages of single-stage MD process. Generally the gained output ratio (*GOR*) evaluating the performance of the single-stage MD is less than 1. However, the *GOR* of the MEMD process can be 20 from literatures. It is even better than multiple-effect evaporation (MEE) and multistage flash (MSF). The MEMD process can significantly increase the thermal energy efficiency and reduce the cost of equipment. Many researchers are trying their best to study the MEMD technology and find out an appropriate process.

The process of a countercurrent direct contact membrane distillation (DCMD) module and a heat recovery heat exchanger was developed in 1987 (Fane et al. 1987). On this basis, different designs for cascade of cross-flow DCMD were developed by Gilron et al. (2007). They theoretically analyzed the influence of the operating conditions such as brine temperature, distillate temperature, and brine flow rate on the performance of MEMD process. Methodologies were presented to maximize energy recovery and show the cost of the cross-flow DCMD stages. The

results indicated that with the optimum number of cross-flow stages, the distillate cost would be competitive with that of large-scale seawater RO.

The MEMD Processes with DCMD Modules

In 2010, a new design was developed by integrating a countercurrent cascade of cross-flow DCMD and a heat exchanger (Lee et al. 2010). The heat exchanger is filled of solid polymeric hollow fibers. A novel numerical simulator was developed to simulate the performances of this device. And an experiment was operated to demonstrate the numerical model. The numerical simulator predicts that the *GOR* can be 12 when the brine flow rate and distillate flow rate are different.

He et al. presented their research about a series of countercurrent DCMD cascades of two types (He et al. 2012). Two different configurations (Fig. 1) with interstage heating or not were theoretically analyzed. The results show that with interstage heating provided at the top of each stage, the energy recovery is about 60 % and *GOR* may be above 20.

The MEMD Processes with VMD Modules

By replacing the flash chambers of MSF desalination systems with membrane distillation modules, a small-scale and off-grid desalination system (Fig. 2) can be built (Edward et al. 2013). The results of model analysis showed that the multistage vacuum membrane distillation (MSVMD) system can achieve the performance of MSF for the same condition. Additionally, MSVMD has some advantages over MSF, such as operation at lower temperature, the use of low temperature heat sources, and the use of inexpensive polymer materials.

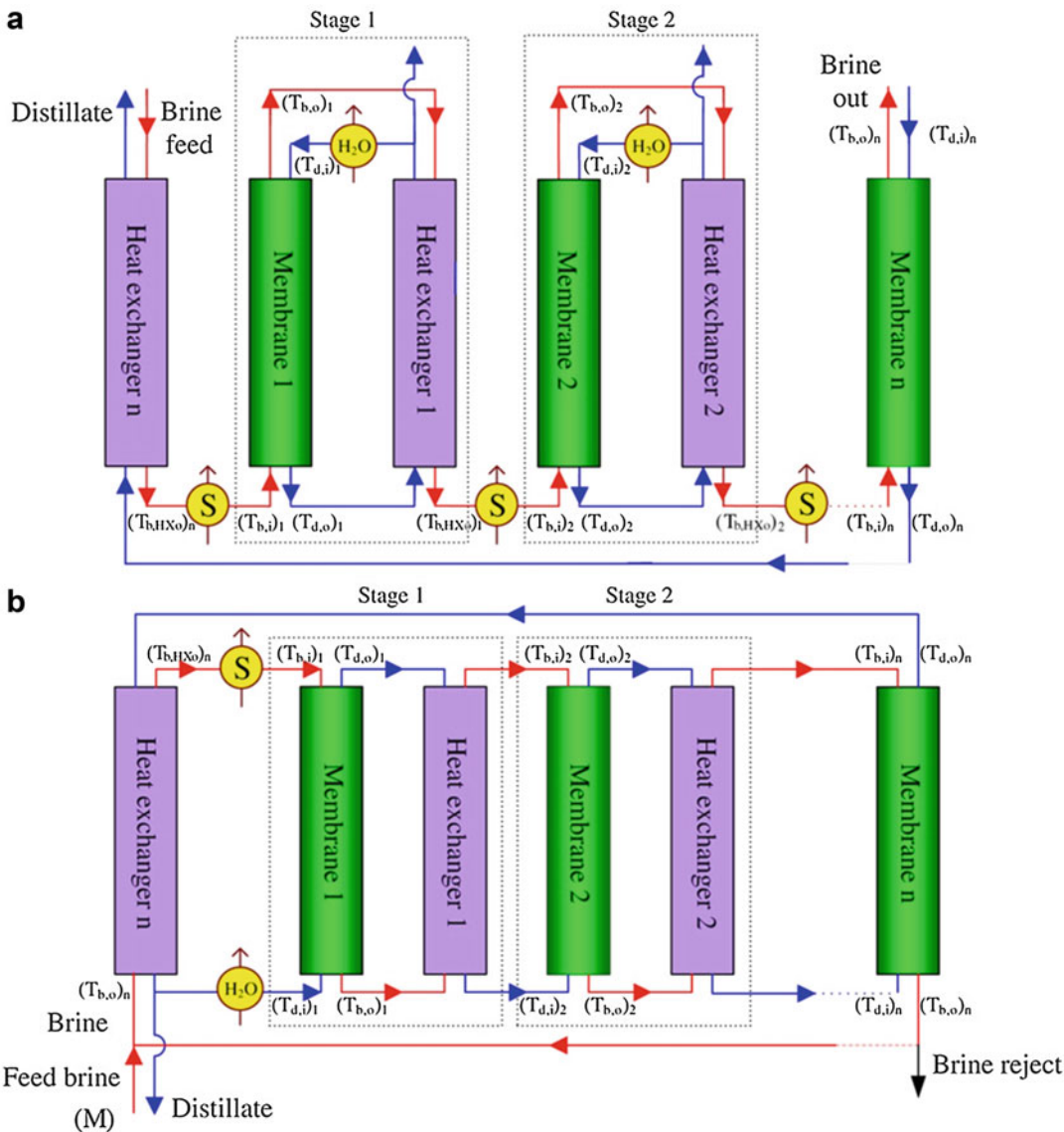
The memsys has developed a novel vacuum multi-effect membrane distillation (V-MEMD) module (Zhao et al. 2013). The V-MEMD process is achieved by many single stages connecting. Every single-stage's structure

includes alternating membrane frames and foil frames for evaporation and condensation. Vacuum enhances the membrane distillation process and solar provides the energy. The results showed that the heating and cooling temperatures are the main factors among the operation conditions affecting flux and energy recovery. Also the optimization of module design shows that the memsys module has great potential in increasing the *GOR*.

The MEMD Processes with AGMD Modules

A method that integrates the heat exchanger network (HEN) into the MD system is presented (Lu and Chen 2012). The schematic diagram of the integrated system of AGMD and HEN is showed in Fig. 3. The waste heat from HEN can be the energy source of the MD process so as to reduce the water cost. The method consists of two steps: first, the stream data is calculated for the MD design; second, HEN design is done. The design results show the optimal multistage MD system that can keep high energy efficiency and improve the productive rate of the system. It also gives the optimal operating conditions and explicit stream data. The cost difference between HENs with and without the MD streams is considered as the partial cost of pure water resulting from the MD process.

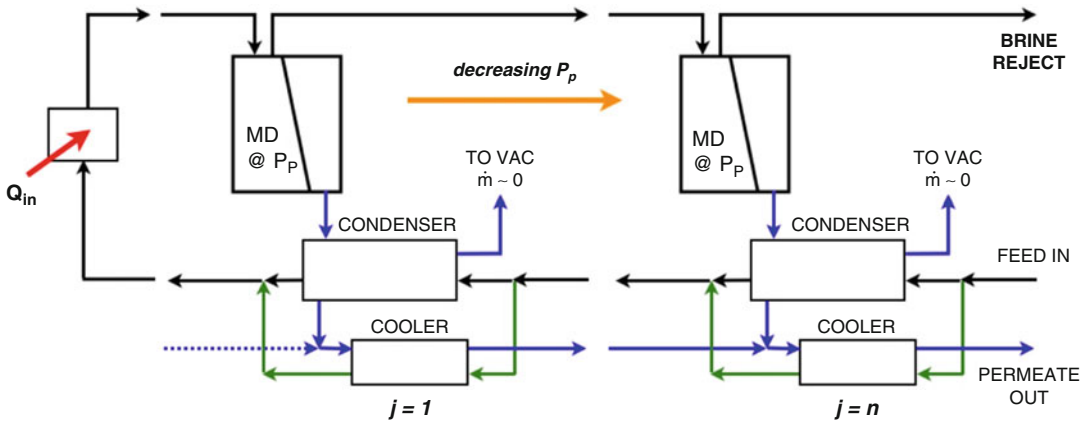
A heat recovery technology in AGMD process using a two hollow-fiber-set membrane module has been developed. In the module, the hot brine flows through a porous hydrophobic membrane, the vapor through the wall of the porous hydrophobic membrane is condensed on the wall of dense wall fibers and warms up the cold brine flow. The configuration of MEMD process is presented in Fig. 4, which includes the AGMD module described before and an external heat exchanger. Enrichment experiment of semi-volatile organic acids from aqueous solutions by this MEMD process has been completed (Ban Rui et al. 2012). The influence of operating conditions for the performance of MEMD process has been studied. The *GOR* of this experiment can be 9.84



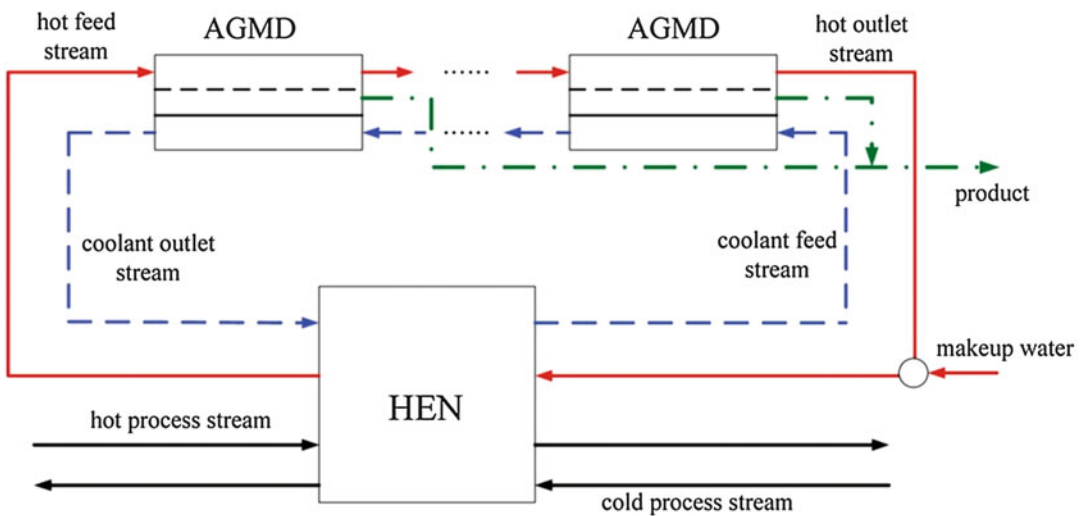
Multi-effect Membrane Distillation, Fig. 1 Two different modes of obtaining increased recovery by operating with a series of cascades: (a) with interstage brine heating and (b) without interstage brine heating

and the acid rejection rate can be 99.93 %. The results present that the MEMD process can be potentially applied to enriching organic acids from their respective dilute aqueous solutions. Using this MEMD process, Xiaojun Li et al. studied the concentration of aqueous sulfuric acid

solution (Xiaojun Li et al. 2012). The *GOR* value obtained was much higher than that in traditional and other modified membrane distillation processes. The maximum value of *GOR* could reach 11.5. And in a long-term stability test (lasting for more than 30 days), the MEMD



Multi-effect Membrane Distillation, Fig. 2 Multistage vacuum MD (MSVMD) process diagram



Multi-effect Membrane Distillation, Fig. 3 Schematic diagram of the integrated system of AGMD and HEN

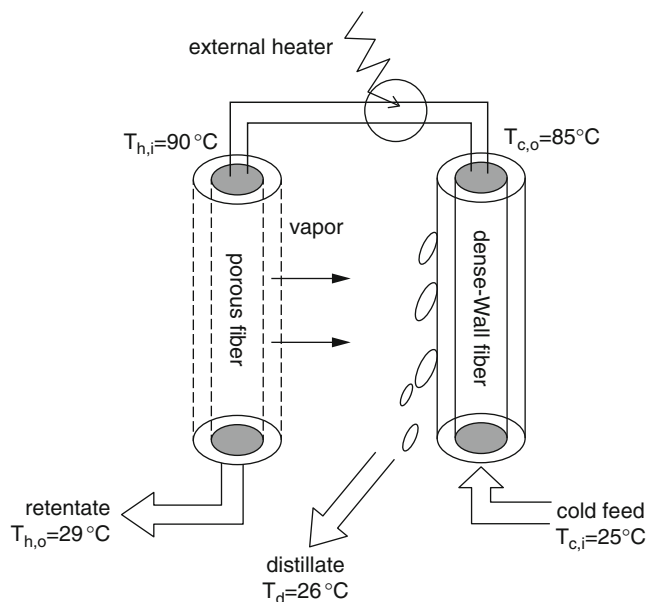
modules were kept in good condition, which demonstrated the stability of this MEMD process.

A conception of continuous-effect membrane distillation (CEMD) was proposed in 2013 Yao et al. (2013). The CEMD process based on hollow fiber AGMD module and the MEMD process with an AGMD module are exactly the same. However, the research studied two kinds of CEMD modules made from

different membrane fibers. The influences of operating conditions on the performance of CEMD process have been investigated. Within the studied experimental range, the maximum *GOR* value could reach 13.8. The theoretical model successfully predicted the possible ways to obtain a higher *GOR* value. And the experiment data showed agreement with theoretical conclusions.

Multi-effect Membrane Distillation,

Fig. 4 Schematic presentation of hollow fiber-based MEMD process



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Multielectron Redox Catalysts

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Multielectron redox reactions play a key role in many biological and synthetic catalytic processes. Multielectron redox processes require the use of a catalyst able to store several redox equivalents. A redox catalyst is a substance which can accept or donate several electrons such that each electron is added or removed at approximately the same potential. When fully charged, the catalyst should be capable of driving a multielectron redox reaction in a process with a few intermediate steps (Fendler and Bolton 1986).

Multielectron redox catalysts function through redox potential leveling (Huynh and Meyer 2007). Redox potential leveling is a process where proton-coupled electron transfer leads to

the accumulation of multiple oxidizing equivalents over a low range of potential (Wang et al. 2010). The additional demand on the catalyst is that it must accumulate and use multiple oxidative equivalents at high redox potentials and carry out a difficult, multielectron reaction or reactions without reacting with itself or its surroundings.

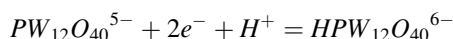
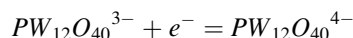
The ability of heteropoly acids (HPAs) and their conjugate anions (polyoxometalates) to perform fast reversible multielectron redox transformations under rather mild conditions prompted interest in the systems as electrocatalysts for various inert redox reactions including hydrogen evolution and oxygen reduction. It has been recognized that the partially reduced heteropolyanions of W and Mo provide highly reactive mixed-valence redox centers. However, nearly all multielectron transfer in polyoxometalates systems is driven by either adding strong reducing and oxidizing reagents into solution or through electrochemical redox reactions (Takashima et al. 2012).

Polyoxometalates can undergo fast and reversible multielectron redox reactions. Electron transfer occurs between mixed-valence transition metal sites according to the electron self-exchange or electron hopping mechanism. This model is operative during partial electroreduction, i.e., injection of up to four electrons to a Keggin-type heteropoly structure of molybdenum and tungsten. Further reduction of heteropolytungstate or molybdate is irreversible and leads to the formation of so-called heteropolybrown species in which such distinct ionic sites as W^{VI} and W^{IV} or Mo^{VI} and Mo^{IV} can coexist (Bard et al. 2008).

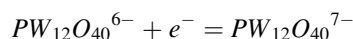
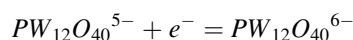
The heteropolyanions undergo several rapid one- and two-electron reversible reductions to produce the so-called “heteropoly blue” and further irreversible multielectron reductions with concomitant decomposition. The electrons are accepted by the addenda ions of the heteropolyanions. If the addenda ions are all identical, the electrons are delocalized on the addenda ion oxide framework at room temperature by rapid electron hopping (intramolecular electron transfer). The reduction increases the negative charge density at the heteropolyanions and thus their basicity.

As a consequence, the reduction can be accompanied by protonation depending on the pK_a of the produced oxometalates (Sadakane and Steckhan 1998).

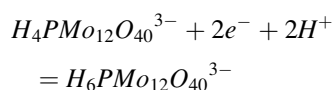
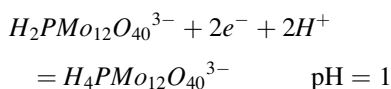
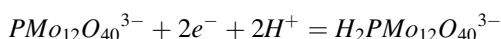
Keggin-type heteropolyanions can accept a limited number of electrons without decomposition, and in some cases the reduced compounds have been isolated.



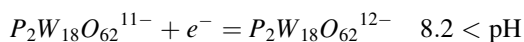
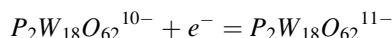
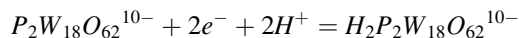
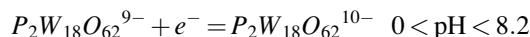
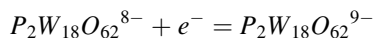
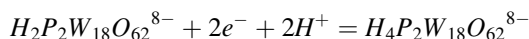
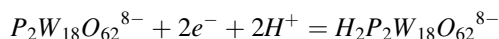
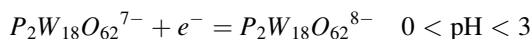
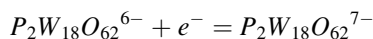
With increasing pH, the third reversible two-electron wave moves to a more negative potential and splits into two reversible one-electron reduction waves at pH 4:



For phosphopolyoxomolybdate, it is difficult to obtain well-defined redox waves in cyclic voltammetry in aqueous electrolytes due to the easy hydrolysis of $PMo_{12}O_{40}^{3-}$. However, it is stabilized by addition of comparatively large amounts of organic solvents. The reduction potentials depend on pH as a result of protonation (Sadakane and Steckhan 1998; Gómez-Romero and Casañ-Pastor 1996).



Dawson-type heteropolyanions undergo several reversible one-electron reductions in organic and aqueous solvents if no protonation accompanies the reductions.



The stability of tungstophosphoric acid in aqueous solutions is considerable dependent on pH with regard to the dominant species present in the solution (Holclajtner-Antunović et al. 2008). Many factors influence the equilibrium, primarily pH and HPA concentration, while the performance of different analytical techniques used for speciation should be taken in account as well. Tungstophosphoric acid decomposes first to components of the Dawson series, while the total decomposition of the Keggin anion to phosphate and tungstate occurs at $\text{pH} > 7.5$.

It should be noted that, besides the ability to perform multielectron redox transformations, HPAs also have a very strong Brønsted acidity approaching superacid region. Their acid-base and redox properties can be varied over a wide range by changing the chemical composition (Damjanović et al. 2005). HPAs catalyze a wide variety of reactions in homogeneous liquid phase. Being stronger acids, HPAs will have significantly higher catalytic activity than mineral acids. HPA catalysis lacks side reactions such as sulfonation, chlorination, nitration, etc., which occur with mineral acids (Kozhevnikov 1998).

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Multifunctional Responsive Membranes

► Magnetically Responsive Membranes

Multilayered Thin Film Composite Membranes

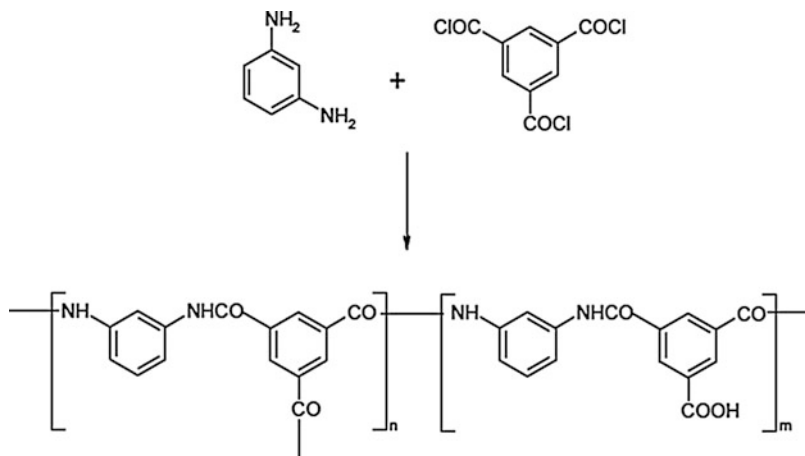
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A thin film composite (TFC) membrane is a bilayer of multilayer membrane constituted by

Multilayered Thin Film Composite Membranes,

Fig. 1 Interfacial polymerization in the formation of thin film composite membranes



an asymmetric porous structure and a thin and dense-selective film. The asymmetric structure gives mechanical stability to the membrane, without restricting flux. It is normally obtained by phase inversion and frequently based on polysulfone. In the most known TFC membranes, the thin layer is based on polyamide and is prepared by interfacial polymerization (Nunes and Peinemann 2006). Having a typical thickness lower than a micrometer, the dense layer gives the needed selectivity for salt (reverse osmosis) or other small solutes, without adding a high barrier for water transport. Interfacial polymerization as a simple and effective method for TFC membranes started to be explored by Cadotte et al. (1980) in the 1960s. Initially polyethylenimine and diisocyanate were used as monomers, resulting in what was known as NS-100 membrane. The most used system for thin film preparation is currently a combination of m-phenylenediamine (MPD) and trimesoyl chloride (TMC), as shown in Fig. 1. The porous asymmetric support is filled with an aqueous solution of MPD and immersed in an organic solution containing TMC (e.g., in hexane). By choosing immiscible solvents, the reactants will only contact each other at the interface. The reaction takes place immediately to form a defect-free polymeric film. Once the film is formed, the monomers are no longer in contact anymore, limiting the thickness. The system in Fig. 1 led to the development of reverse osmosis membranes such as FT-30,

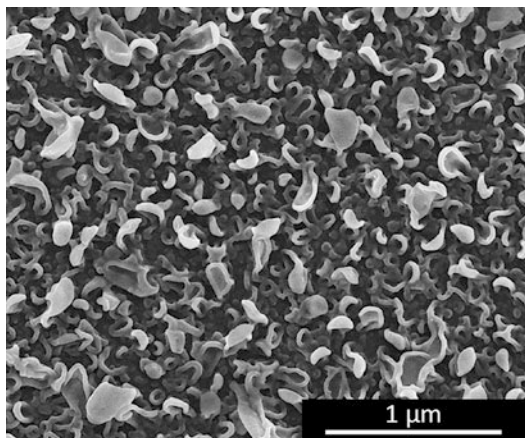
commercialized by Dow, which has dominated great part of the desalination market with salt rejection higher than 99.2 % and fluxes of around $1 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$.

Comprehensive reviews on thin film composite membranes for reverse osmosis and nanofiltration were published by Petersen (1993) and, more recently, by Lee et al. (2011).

Despite of the success of the polyamide membranes shown in Fig. 1, a drawback is still the chlorine resistance, which was also poor for the NS-100. Other chemical compositions have been proposed over the years to improve resistance, such as polypiperazine-amide-based films. However, the overall combination of high flux and salt rejection is the most important target. The development of TFC membranes had a strong contribution to the widespread implementation of desalination plants from seawater.

TFC membranes are now applied also for emergent processes such as forward osmosis and pressure retarded osmosis. The requirements for these applications are different, which operate at much lower pressure than reverse osmosis (RO). High flux is even more important. While the resistance to compaction is not as important as for RO, an opener support is desired to avoid accumulation of draw solutes in the membrane and concentration polarization effects.

A typical ridge-and-valley structure is observed on TFC membranes, as seen in Fig. 2.



Multilayered Thin Film Composite Membranes, Fig. 2 Scanning electron microscopy image of a polyamide TFC membrane

The morphology of the thin layer is affected by the porosity of the substrate. Larger pores can promote convection at the interface during the polymerization and a rougher structure. Changes in the monomer concentrations and addition of solvents of intermediate miscibility affect the morphology and thickness, as well as the integration of hydrophilic intermediate layers (Livazocic et al. 2015). More recently TFC has been applied to filtration in organic solvents (Karan et al. 2015) reaching permeances of more than $112 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$.

Apart from the thin film composite membranes prepared by interfacial polymerization, other methods can be used to form a selective layer leading to composite membranes:

- (a) Dip coating of a diluted polymer solution on a porous support, followed by solvent evaporation
- (b) Film deposit by plasma
- (c) Separated casting, delamination, and deposit on a support
- (d) Dip coating of a monomer solution, followed by reaction (e.g., by UV radiation or heat)

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Multiphase Enzyme Membrane Reactors

► Biphasic Biocatalytic Membrane Reactors

Multiple Emulsions

► Double Emulsion

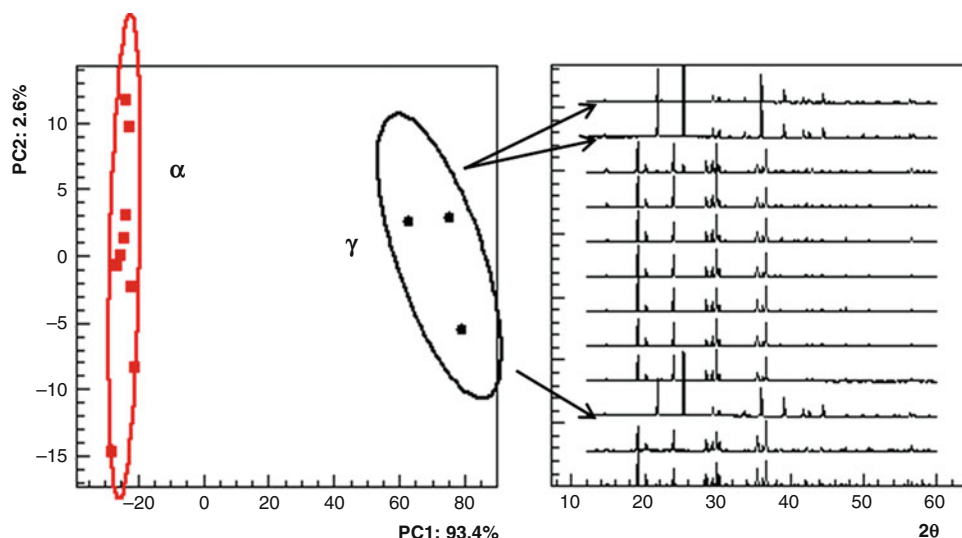
Multivariate Analyses

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Multivariate analysis techniques allow more than two variables to be analyzed at once. Two general types of techniques exist: (i) analysis of interdependence, where no variables are thought of as dependent. These methods look at the relationships among variables and are unsupervised. (ii) Another is analysis of dependence, where one or more variables are dependent variables, to be explained or predicted by others. These methods are supervised and typically are constituted by multiple regression.

Data, for example, acquired spectra, are arranged into a table (matrix) in such a way that each row represents one sample and each column



Multivariate Analyses, Fig. 1 Score plot of the first two principal components and related X-ray diffraction profiles of glycine polymorphs produced in membrane crystallization experiments. 90 % confidence level ellipsoids are drawn

one measured variable (Kvalheim 1988). When the number of variables increases, the challenge is to find low-dimensional, information-rich projections of both variable and sample space since the full spaces cannot be displayed and comprehended in a simple manner. This task can be achieved by projecting onto latent variables (Rajalahti and Kvalheim 2011). The oldest and most common latent variable projection method is ► **Principal Component Analysis** (PCA) (Jackson 1991; Wold et al. 1987). The data matrix $\mathbf{X}$ is decomposed into a number of principal components (PCs) that maximize explained variance in the data on each successive component under the constraint of being orthogonal to the previous PCs. An example is given in Fig. 1, where clear classification of glycine polymorphs obtained by membrane crystallization processes is achieved by applying PCA to X-ray diffraction data (Di Profio et al. 2013). Drawbacks of PCA are that the criterion for the latent variables does not always guarantee the perfect separation among group of data and that it cannot be applied for quantitative analysis.

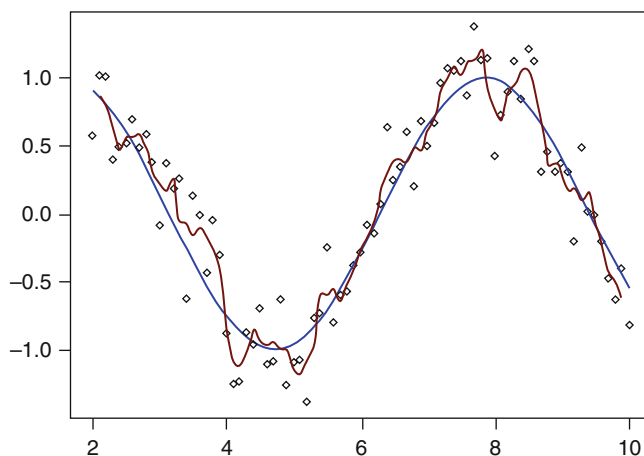
Supervised regression methods are instead used to build a model to interpret data and to produce predictions by using such model. Regression is a mathematical method for determining the

best equation that reproduces a data set, and it is supervised because input data are divided into two subgroups: a training or calibration set, from which data are used to estimate model parameters, and a test or prediction set, from which data are used to get an independent assessment of model efficacy and to produce predictions. Regression models should avoid data over-fitting (see, e.g., Fig. 2), which occurs when a surplus of parameters causes an over-interpretation of the calibration set, with a consequent poor efficacy in predicting outputs for the prediction set. The most common regression method is Least Square Fitting, where the best fit of a function (model) to experimental data is found. The fitting is based on the minimization of the sum of the squared residues between model and experimental data. Another widespread method is Partial Least Squares, where the dependent variable Y is filled by known responses for the calibration set and with predicted ones for the prediction set. The regression model is built by finding the maximum covariance between Y and the independent variable X .

Performances of multivariate techniques can be enhanced by data pre-processing, which are specific for the kind of data, and produce rescaled data from original ones. Common pre-processing

Multivariate Analyses,

Fig. 2 Example of over-fitting in regression. True (blue line) and estimated (red line) trends are superimposed to experimental data (empty circles)



techniques are mean centering, standard normal variate, normalization, and background subtraction.

Vibrational spectroscopy, such as infrared, near infrared, and Raman, X-ray diffraction, and imaging techniques are characterization methods that have been applied in membrane technology applications to monitor physical and chemical phenomena occurring during the processes. These techniques produce data with high dimensionality, since each sample is described with hundreds or even thousands of variables.

Multivariate methods can play a critical role in process understanding, multivariate statistical process control (MacGregor and Kourti 1995), fault detection and diagnosis, and process control and process scale-up.

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Multivariate Image Analysis (MIA)

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MIA was originally proposed in the late 1980s (Geladi et al. 1989; Esbensen and Geladi 1989; Geladi and Esbensen 1989). It consists basically in the application of multivariate chemometric methods to enhance the quality of images that has usually been obtained using spectra recorded over a range of wavelengths. A digitized image is usually composed of pixels, which are small “dots” on the screen. Each pixel contains some information presented normally as a color of a given intensity on the photographic or microscopic image. The image can be unfolded and so treated as a long data matrix, with one dimension corresponding to all the pixels in the image and the other to the wavelength ranges or spectra. Generally, this matrix is then transposed so that the pixels represent rows and the columns spectral

frequencies. This provides an unsupervised classification of the image pixels based on their spectral signature which can be observed in the score space $\mathbf{T}$ of the PCA model. The information contained in the image is then explored and interpreted by iteratively segmenting regions of interest in the image feature space $\mathbf{T}$ (i.e., PCA score space) and overlaying the identified pixels on the original image scene. This is often referred to as the masking procedure by which spectral features are extracted from the image (Brereton 2007).

MIA involves a series of steps from image acquisition to obtain the desired information (i.e., prediction, monitoring, and control schemes). After acquiring digital images (e.g., infrared-IR, Raman microscopy, satellite images, NMR, medical images, X-ray, or near-infrared images), these should be preprocessed or filtered to enhance the image quality as well as to remove irrelevant sources of variation. Subsequently, a vector of relevant features is extracted from each image. This step is definitely the most critical part of the framework, due to sensitivity and robustness of the final machine vision system which strongly depend upon the responsiveness of the features to the desired information to be obtained from the analysis. Therefore, it is required to determine the type of features to investigate, i.e., spectral features, textural features, or a combination of both. The key issue of this step is to determine if the desired information is proportional to the number of pixels, colors, or spectral signatures. The traditional approach for extracting features from multivariate images consists of iteratively segmenting the score density histograms (i.e., masking in the feature space $\mathbf{T}$) and overlaying the selected pixels in the original image space where the segmentation quality is assessed. In this approach, the masks in the feature space $\mathbf{T}$ are adjusted by trial and error until satisfactory segmentation of the image is achieved. Since no $\mathbf{Y}$ data is used in the masking procedure, a priori knowledge of the objects to be captured in the image space is required (Duchesne et al. 2012).

Posteriorly, image features are analyzed by using empirical models such as principal

component analysis (PCA), partial least square (PLS), and partial least square discriminant analysis (PLS-DA). PCA has been used for unsupervised image classification. For further classification analysis, incorporating class data, PLS-DA can be used. On the other hand, when the objective is to build inferential models for process response variables or product properties $\mathbf{Y}$ (i.e., membrane characteristics), MIA based on PLS provides predictions, after previous model calibration and validation.

Several applications of MIA have been reported in various fields such as the analysis of pharmaceutical tablets to determine the distribution of excipients and active drugs, associated at properties like solubility (Brereton 2007). Other applications are focused on multivariate images obtained from fields of remote sensing (satellite imagery) (Esbensen and Geladi 1989), analytical chemistry (e.g., NMR) (Geladi and Grahn 1996), and medical imaging (e.g., MRI) (Geladi and Grahn 1996). Application of MIA in the process industries is more recent. Bharati and MacGregor (1998) advocated the use of MIA for online process monitoring by applying the method to a time series of images. Since process images are generally acquired in a sequence, computing the number of pixels having a specific spectral signature (i.e., falling under a mask) in each image of the sequence could be useful to monitor the frequencies of occurrence of certain abnormal process events or product defects (Bharati and MacGregor 1998).

The application of MIA approach to membrane characterization is an interesting challenge not yet covered. Membrane images can be used for predicting various response variables ($\mathbf{Y}$) such as pore size, pore size distribution, thickness, water permeability, selectivity, etc.

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Nanoclays

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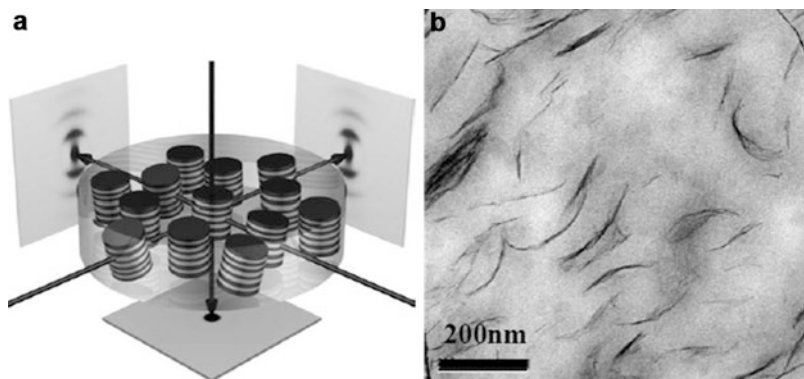
Nanoclays are mainly formed from volcanic ash or rocks with unique layered structure. Typically, silica and alumina are the dominant constituents of clays, with two types of sheeting structure as silica tetrahedral and alumina octahedral sheets. Each clay layer includes two tetrahedral sheets and one octahedral sheet. The silica tetrahedral sheet consists of SiO_4 groups linked together to form a hexagonal network, while the alumina sheet consists of two planes of close-packed oxygens or hydroxyls between which octahedrally coordinated aluminum atoms are imbedded. The two tetrahedral sheets sandwich the octahedral, sharing their apex oxygens with the latter. One of the major family members in nanoclays is natural montmorillonite, generically referred to as nanoclay, which is mainly used to create nanocomposite with polymer materials such as nylon 6 (Picard et al. 2007). We assume the

individual nanoclay stack possesses cylindrical symmetry about its stack axis, and the axes of all the nanoclay stacks are preferentially oriented with respect to the film normal. In other words, the film possesses fiber symmetry as illustrated in Fig. 1a. For the edge-on scattering geometry, it will refer to the vertical direction as the “meridional” direction and the horizontal direction as the “equatorial” direction. For a system with moderate orientation of nanoclay stacks, the meridional scattering in the edge-on SAXS is arc-like, which can be factored into a radial and an angular component. Figure 1b reveals that there is no large aggregation of nanoclay stacks in the polymer matrices, and the homogeneous dispersion of nanoclays in the polymer matrix is achieved. The polymer chains penetrate in between the layers of the nanoclays and break them into individual sheet (Nawani et al. 2010).

The polymer/nanoclay nanocomposite membranes are mainly applied in gas separation, pervaporation, and fuel cell system, where the nanoclay is used to improve the proton conductivity, gas diffusion, methanol permeability, as well as mechanical properties of the membranes (Alonso et al. 2009; Marras et al. 2008; Anilkumar et al. 2008; Frounchi et al. 2006).

Nanoclays,

Fig. 1 Directional 2-D SAXS images simulated from disk-like nanoclays with cylindrical symmetry and preferred orientation (**a**) and a typical TEM image of polymer/ montmorillonite nanocomposite (**b**) (Nawani et al. 2010)



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Nanocomposite Membranes

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Synonyms

Mixed matrix membranes (MMMs)

Nanocomposite membranes or mixed matrix membranes (MMMs) are heterogeneous membranes having inorganic particles dispersed into polymeric matrices, with the aim of improving the performance of membranes by synergistic combinations of the properties of both components. The nanocomposite materials possess enhanced properties compared with the single organic or inorganic material. Such improvement is either with respect to separation performance (higher selectivity and permeability) or to physicochemical properties (hydrophilicity, porosity, charge density, and mechanical, optical, electrical, and thermal properties). In addition, the introduction of nanoparticles into organic polymers can improve the resistance to chemical reagents and antifouling properties in the water treatment processes.

Nanocomposite membranes appear as an interesting approach for overcoming the problem of the trade-off relationship between selectivity and permeability of the pure polymeric membranes (Robeson 2008). The properties of polymer composites depend on the nanoparticles that are incorporated, including their size, shape, concentration, and interactions with the polymer matrix. Numerous polymers, both in glassy and rubbery states, have been studied as continuous matrices in MMMs. Some glassy polymers were investigated including perfluorinated materials, polyimides, polysulfone, polyetheretherketone, and polymer of intrinsic microporosity (PIM-1). Rubbery polymers are also attracted as continuous matrices such as silicone, polyethylene, and polybutadiene. Often natural polymers (polysaccharides, collagen, and chitosan) are

also employed as the matrix. Nanoparticles of various natures were embedded in the polymer matrix. They have been widely used in optical, electrical, and magnetic fields. Nanoparticles consist of conventional fillers (zeolites, carbon molecular sieves (CMSs), silicas, and metal oxides) and alternative fillers (carbon nanotubes (CNTs), metal organic frameworks (MOFs), graphenes, and layered silicates) (Rezazazemi et al. 2014). The successful implementation of nanocomposite membrane depends on the dispersion and distribution of fillers in the continuous phase as well as for the interface compatibility between the particles and the polymer. The homogeneous dispersion of nanoparticle in composites is a challenge because of the immiscibility of polymer and nanoparticles due to a missing interaction. Therefore, it is necessary to modify the particles to overcome their tendency to aggregate and improve their dispersion in polymer matrices. The main defects at the polymer-particle interface, including interfacial voids or sieves-in-a-cage, rigidified polymer layer around the particles and finally the particle pore blockage. Surface modification of inorganic particles is a popular technique because it produces excellent integration and an improved interface between inorganic filler and the polymer matrix. There are two main approaches for modification of the surface of the nanoparticles: modification of the surface of the inorganic particles by chemical treatment and grafting of functional polymeric molecules to the hydroxyl groups existing on the particles (Hong and Chen 2015). Basically there are three general ways to prepare nanocomposite membranes, including: sol-gel process, *in situ*/interfacial polymerization and phase inversion method (Souza and Quadri 2013).

The *sol-gel* technique is the method most applied for the preparation of polymer-inorganic nanocomposite membranes with highly homogeneous and controlled morphology. In this method, organic monomers, oligomers, or polymers and inorganic nanoparticle precursors are mixed together in the solution. The inorganic precursors then hydrolyze and condense into well-dispersed nanoparticles in the polymer matrix.

Nanocomposite Membranes, Table 1 Several nanocomposite membranes and their applications

Polymer matrix/fillers	Application	Aim
Poly(butadiene)/MgO	Gas separation	Increasing CO ₂ permeability
Polyamide/CNTs	Reverse osmosis	Antifouling and antioxidant properties
		Improving flux
Poly(lactic acid)/graphene oxide	Packaging	Enhancement gas barrier performance
Nafion/CNTs	Fuel cell	Increasing electronic conductivity
Chitosan-gelatin/ZnO	Biomedical	Antibacterial and improving mechanical properties
Poly(vinyl alcohol)/zeolitic imidazolate frameworks (ZIF-8)	Pervaporation	Improving flux

In *in situ*/interfacial polymerization, the nanoparticles are well mixed with organic monomers, and then the monomers are polymerized. There are often some functional groups such as hydroxyl or carboxyl on the surface of the inorganic particles, which can generate initiating radicals, cations or anions under high-energy radiation, plasma, or other circumstances to initiate the polymerization of the monomers on their surface.

In the *phase inversion method*, the preparation of nanocomposite membranes can be grouped by the following general procedure:

- Separate preparation of a polymer solution and a suspension of inorganic material.
- Mixing of both resulting in a mixed matrix solution.
- Casting solution is cast as film (or spinning) followed by phase inversion process. It can be induced by evaporation of solvent, immersion precipitation using nonsolvent, or by thermal precipitation.

The development of nanocomposite membranes finds applications in different fields such as gas separation, pervaporation, fuel cell, packaging, and water and wastewater treatment. In addition, nanocomposite membranes are of huge interest to biomedical technologies such as controlled drug delivery, tissue engineering, dental applications, and bone replacement/repair. In Table 1 are reported some types of nanocomposite membrane and their applications.

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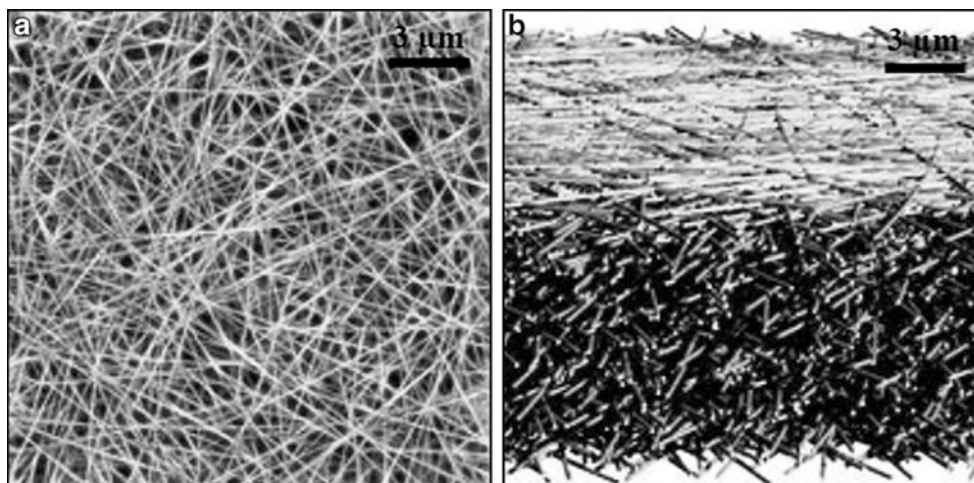
Nanofiber

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Nanofibers are fibers with a nanoscale fiber diameter. They can be fabricated from a variety of natural or synthetic, inorganic, organic, or polymeric materials by using a range of technologies, with the most common example being electrospinning, which has been developed rapidly in recent years to fabricate mainly nanofibers from polymeric materials. In the early 1900s, Cooley and Morton invented electrospinning, based on Gray's observation of water behavior under the influence of electrostatics (Teo and Ramakrishna 2006). During the electrospinning process, a

polymer solution is charged and is flowed out of a spinneret, and a droplet is formed under an external electrostatic field. By increasing the applied voltage to be strong enough to overcome the surface tension of the polymer solution, a fine jet is ejected from the tip of the droplet, which now has a cone-shaped form, known as the Taylor cone. When the jet stream travels from the spinneret to the collector, the solvent is being evaporated, and a nonwoven fibrous scaffold is formed on the collector. The fiber diameter and the morphology of the nonwoven mat are affected by (1) both processes: how the jet is formed and what occurs when the jet stream travels from the spinneret to the collector; (2) the material parameters, such as solution properties (concentration, viscosity, and conductivity as well as nature of the polymer and that of the solvent used); (3) and processing parameters, such as applied voltage, solution flow rate, and distance between the spinneret tip and the collector, as well as temperature, humidity, etc. More and more researchers in the fields of nanoscience and nanotechnology have gradually realized the important potentials of this process, resulting in a flourishing of activities. One main attractive feature of electrospinning is the ability to fabricate nanoscale polymeric fibers from (sub)micron diameters down to nanometer diameters with potential advantages, such as large surface area per unit mass. Electrospun fibrous scaffolds can offer a broad range of applications, including (1) tissue engineering, (2) drug delivery, (3) filtration and gas storage, and (4) sensors and electrodes for use in electronics (Huang et al. 2003).

As an applications example of nanofibrous membranes, the electrospun nanofibrous membrane can be used to remove bacteria, viruses, dyes, and toxins through size exclusion and adsorption from contaminated water. The membranes possess higher permeation flux and lower pressure drop performance than conventional microfiltration membranes. Moreover, the high surface-to-volume ratio and the ability to functionalize the surface of nanofibers permit those membranes to remove toxic metal ions with a capacity comparable to those of typical absorbents (Ma et al. 2013) (Fig. 1).



Nanofiber, Fig. 1 Representative electrospun nanofiber scaffolds with (a) top view and (b) cross-sectional view (Ma et al. 2013)

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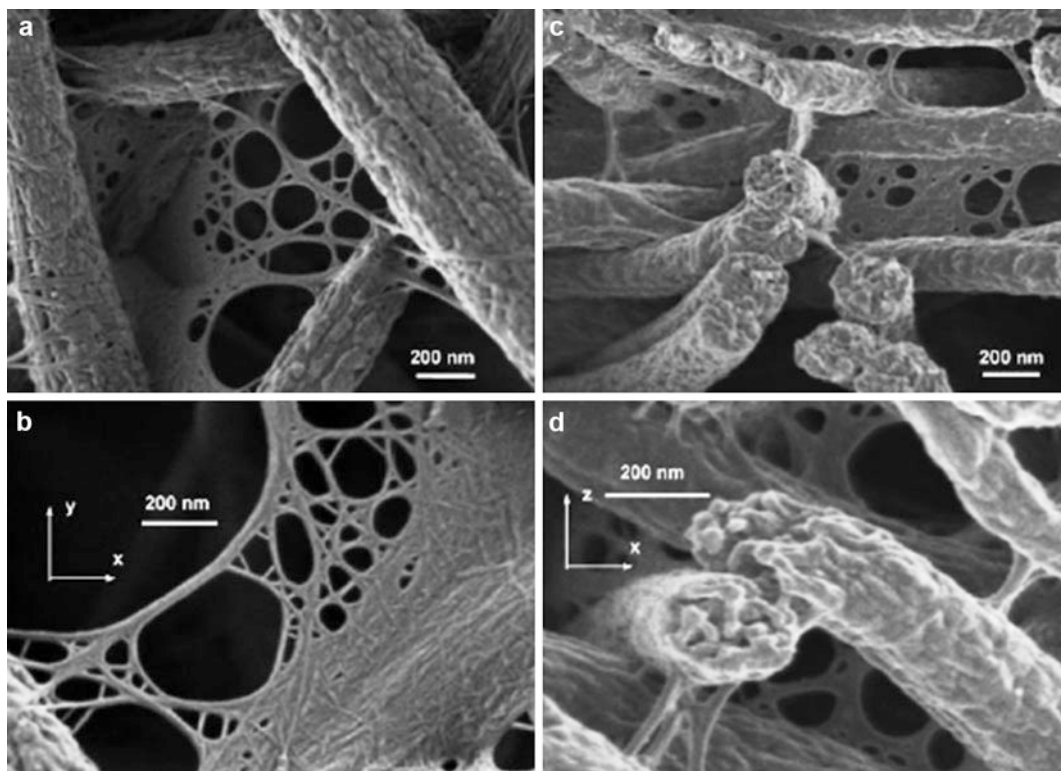
Nanofibrous Microfiltration Membranes

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Nanofibrous microfiltration membranes are fibrous membranes with nanofibers acting as the barrier layer in a microfiltration process. Typically, the membrane has a two-tier structure, with a nonwoven fibrous mat as the substrate support layer, partially also for mechanical strength, and an electrospun nanofibrous scaffold as the top barrier layer, which can selectively

retain targets, either by size exclusion or surface adsorption from contaminated water resources.

A highly permeable nanofibrous microfiltration membrane has been designed and fabricated by using nonwoven polyethylene terephthalate (PET) mat as the substrate and an electrospun polyacrylonitrile (PAN) nanofibrous scaffold being deposited onto the substrate and with an option to have immobilized cellulose nanofibers deposited on the *surface* of PAN nanofibers by impregnation (Ma et al. 2011). The cellulose nanofibers are collapsed onto the surface of PAN nanofibers, forming a fibrous network with high degrees of adsorption sites (Fig. 1). The introduction of cellulose nanofibers tremendously increases the effective surface-to-volume ratio of the electrospun nanofibrous membrane. The surface of electrospun nanofibers can now have a negatively charged property, due to the carboxylate groups on the surface of cellulose nanofibers. Yet, the high porosity characteristics of the electrospun scaffold remain, as the fiber diameter of the electrospun membrane increases only slightly by adherence of the cellulose nanofibers onto those electrospun membranes. The integrated hierarchical structure with fiber diameters, ranging from microns to nanometers, now produces a membrane with high filtration efficiency including both high throughput and retention of specifically targeted species by a



Nanofibrous Microfiltration Membranes, Fig. 1 Nanofibrous microfiltration membrane impregnated with cellulose nanofibers (Sato et al. 2011)

combination of size exclusion and adsorption. The pore size of the membrane can be correlated with the fiber diameter forming the (electrospun) nanofibrous membrane (Ma et al. 2012), whereas the infused cellulose nanofibers offer the adsorption capability. Therefore, cellulose nanofibers can be used to bring two different filtration mechanisms, e.g., size exclusion and adsorption, in the filtration performance of nanofibrous membranes. The nanofibrous microfiltration membrane exhibits 0.2 μm in mean pore size, which could be employed to take out waterborne bacteria, such as *E. coli*, from contaminated drinking water with full retention, as well as positively charged viruses, dyes, and heavy metal ions, simultaneously.

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Nanofiltration

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Nanofiltration (NF) belongs to the class of pressure-driven membrane processes for liquid-phase separations, which also includes microfiltration (MF), ultrafiltration (UF), and reverse osmosis (RO). The four processes make

Nanofiltration, Table 1 Positioning of NF within the pressure-driven membrane processes and its characteristics

Membrane processes	RO	NF	UF	MF
MWCO ^a		200–1000 Da	3–300 kDa	
Pore diameter	<0.5 nm	0.5–2 nm	2–100 nm	0.1–10 μm
Rejection of	Ions	Multivalent ions and molecules	Macromolecules and colloids	Microorganisms, particles, and colloids
Permeation of	Solvents	Solvents, monovalent ions and small molecules	Solvents, mono- and multivalent ions, and small molecules	Solvents and dissolved species
Pressure range (bar)	30–100	5–40	2–10	0.1–2
Osmotic pressure	High	Intermediate	Low	Negligible
Permeate volume flux ($\text{L h}^{-1} \text{m}^{-2}$)	10–70	40–100	50–500	100–1500

^aMWCO designates the molar mass of the smallest component that will be retained with an efficiency of at least 90 %. 1 Da = 1 g mol⁻¹

use of a hydrostatic pressure gradient to generate mass transfer and selective transport of chemical species through synthetic membranes and also to overcome the feed solution's osmotic pressure. They are distinguished by the size of the pores or species to be separated, the applied pressures, the permeate fluxes, etc. (Table 1). NF lies between UF and RO, and its applications thus combine the lower pressures and higher permeate volume fluxes of UF with the high retention of RO.

With pore sizes of the order of the nanometer, NF membranes can therefore retain species with very low molecular weight such as sugars, dyes, organic micropollutants, etc. They are also able to retain ions and exhibit a high selectivity between mono- and multivalent ions. This results from the combination of pore diameters of a few nanometers with electrically charged materials. Indeed, most NF membranes possess a fixed charge that results from dissociation of surface groups (such as carboxylic or sulfonic acids) when they are in contact with polar solvent and/or by adsorption of charged species. Since NF membranes have pore sizes of the same order of magnitude as the distances of action of electrostatic forces, ion exclusion mechanisms are affected not only by steric effects, which are due to the size differences between pores and solutes, but also by

electrostatic interactions involving the Donnan and dielectric effects.

Today, NF is mainly applied in drinking water purification process steps, such as decoloring, micropollutant removal, and water softening. Other applications of NF are separation of dye from textile effluents (Chakraborty et al. 2004), wastewater recycling in laundries, rinse water recycling in plating industry (Frenzel et al. 2006), removal of pesticides and herbicides from groundwater (Kiso et al. 2000), concentration/purification of pharmaceutical broths (Christy and Vermant 2002), concentration of antibiotics (Zhang et al. 2003), and concentration/desalination of lactoserums (Guizard 2000).

Most NF membranes are thin-film composite membranes of organic (polymeric) or inorganic (metal oxides) nature. They are commonly made of three distinct layers prepared from different materials, each having a particular role: (i) a macroporous support layer with a thickness of approximately 100–200 μm for organic membranes and 1–2 mm for inorganic ones, providing mechanical strength while allowing high liquid fluxes; (ii) an active layer whose thickness varies from ~ 10 to ~ 300 nm for organic membranes and being a few microns for inorganic membranes, which is responsible for the separation; and (iii) an intermediate thin layer of high permeation

allowing the deposition of the active layer and preventing the penetration of the latter in the macroporous support during the filtration process. Beyond this common structure, NF membranes have specific physical and chemical features related to their organic or inorganic nature. There is a large diversity of NF polymeric membranes, but cellulose esters, aromatic polyamide, and polyethersulfone are mainly used. Depending on the materials thereof, organic membranes can be used in a pH range from 2 to 11 and at temperatures less than 90 °C. They are sensitive to oxidizing agents, solvents, and surfactants. In general, they possess a negative fixed charge that results from dissociation of surface groups. Inorganic NF membranes are (mixed) oxides, generally of aluminum, zirconium, or titanium. Due to their material properties, they have very good chemical ($1 < \text{pH} < 14$) and thermal stability (maximum working temperature: 350 °C for TiO_2 , 400 °C for ZrO_2 , and higher than 900 °C for $\text{Al}_2\text{O}_3\text{-}\alpha$). An important property of these membranes is the amphoteric character of their surface hydroxyl groups (positively or negatively charged surface sites depending on whether pH is less or larger than the isoelectric point of the material) which allows to control the sign and the charge of the membrane by pH control.

NF membranes are mounted into modules that allow for convenient assembly and operation in modular systems. Polymer membranes are mainly set in spiral wound and tubular modules coming from technologies already mastered in the manufacturing of pressure-resistant RO modules. Changes in spacer grids have been made by some spiral wound module manufacturers in order to increase the turbidity level allowed in the modules. In the case of ceramic membranes, the design of the modules is similar to the one for MF and UF membranes but improved sealing systems enable to reach higher working pressures.

As for RO or UF, typical NF process operating steps include assembly, water flush, integrity testing, buffer flush, processing, recovery flush, cleaning, sanitization, disassembly, and storage.

Manufacturers of NF membranes in 2013 include Danske Separation System AS (DSS AS), Dow/Filmtec, Hoechst (French company Hoechst

and Hoechst Aktiengesellschaft, Separation Products), Koch Membrane Systems Inc (Koch International), Lenntech, Nitto Denko Hydranautics, Novasep, Osmonics (Desal-Osmonics-Autotrol SA; Desalination Systems Inc), PCI Membrane Systems Ltd (PCI, Guerin SA), Permionics, Polymem SA, Stork Friesland B.V., Tami Industries SA, and Vladipore ZAO NTC.

Cross-References

- [Donnan Effect](#)
- [Ultrafiltration \(UF\)](#)

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Nanofiltration (Transport Phenomena)

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Nanofiltration membranes are characterized by effective pore diameters ranging from ~ 1 nm to a few nanometers, and most of them acquire an electric charge when brought into contact with a polar

medium. The combination of nanometric dimensions pores with electrically charged materials implies that the separation of solutes results from complex mechanisms that may include steric hindrance and Donnan, dielectric, and transport effects.

NF membranes are usually described as a bundle of capillaries with effective structural features (pore size and thickness-to-porosity ratio) and electrical properties such as their effective volume charge density (defined as the number of moles of fixed charges per unit of pore volume). The standard theory of NF is based on a macroscopic description of transport, which is actually a simplified version of the so-called space charge model originally developed by Osterle and co-workers (Morrison and Osterle 1965; Gross and Osterle 1968; Fair and Osterle 1971). Within very narrow pores such as those of NF membranes, the electrical double layers cannot fully develop and overlap strongly. As a result, both the local electric potential and ion concentrations are almost radially constant (provided the electric charge carried out by the pore walls is not too high (Szymczyk et al. 1999)). Neglecting these variations yields the so-called homogeneous approximation. This approximation considerably decreases computational effort and is currently used in most studies devoted to transport modeling through NF membranes (Tsuru et al. 1990; Bowen et al. 1997; Wang et al. 1997; Palmeri et al. 1999; Yaroshchuk 2001; Labbez et al. 2002; Bandini and Vezzani 2003; Lefebvre et al. 2004; Lefebvre and Palmeri 2005; Oatley et al. 2005; Szymczyk and Fievet 2005; Déon et al. 2007).

Within the scope of the homogeneous model, the solute separation process is described in three steps. The first one is the solute partitioning at the interface between the feed solution and the pore inlet. Next, the transport of solutes through the membrane pores is considered. Finally, the last step is the partitioning of solutes at the interface between the membrane and the permeate. During the last decade, several transport models have been developed which mainly differ from each other by the equation used to describe the partitioning of solutes at the membrane/solution interfaces. However, all are based on the extended

Nernst–Planck (ENP) equation (Schlögl 1964) to describe the solute transport through the membrane. This equation describes solute transport in terms of diffusion under the action of the solute concentration gradient, migration under the action of a spontaneously arising electric field (in the case of charged solutes only), and convection due to solvent flow. The electric potential gradient arising to fulfill the zero electric current condition at steady state plays a substantial role in the transport of charged solutes through pores because it acts differently on cations and anions. Indeed, the spontaneously arising electric field enhances the molar flux of coions in the permeate direction whereas it diminishes that of counterions so as to allow the transfer in stoichiometric proportions of both species into the permeate compartment.

The ENP equation is frequently modified by hydrodynamic coefficients so as to take into account the effect of the finite pore size on both diffusion and convection (Deen 1987). Assuming that no direct coupling between ionic fluxes occurs (i.e., mutual friction between solutes is neglected (Hoffer and Kedem 1967)), the modified ENP for solute i reads as follows:

$$j_i = -K_{i,d}D_{i,\infty}\frac{d\bar{c}_i}{dx} - \frac{z_i\bar{c}_iK_{i,d}D_{i,\infty}F}{RT}\frac{d\psi}{dx} + K_{i,c}\bar{c}_iV \quad (1)$$

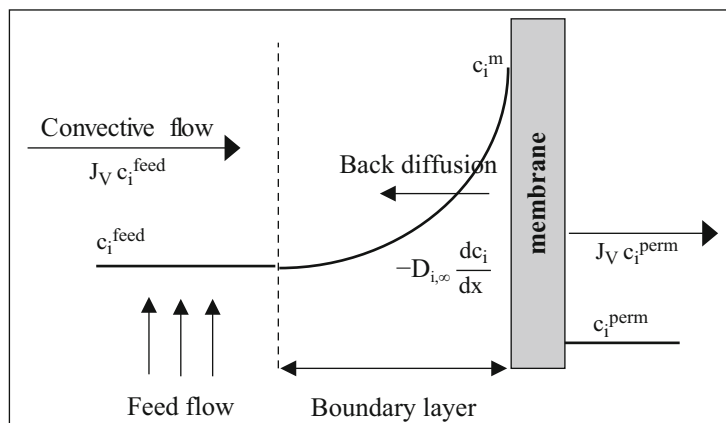
where j_i is the molar flux of solute i through the pores, $D_{i,\infty}$ its diffusion coefficient in the external solution (value at infinite dilution), $\bar{c}_i$ its concentration inside the pores at the x position along the pore, z_i its charge number, ψ the local electric potential inside the pores, V the solvent velocity inside the pores, $K_{i,d}$ the hindrance factor for diffusion inside the pores, $K_{i,c}$ the factor accounting for the effect of pore walls on the solute convective flux, R the ideal gas constant, and T the absolute temperature.

The three terms on the right-hand side of Eq. 1 represent the diffusive, electromigrative, and convective components of the molar flux j_i , respectively.

Hydrodynamic coefficients $K_{i,c}$ and $K_{i,d}$ depend on the ratio of solute to pore radius ($\lambda_i = r_{i,s}/r_p$, where $r_{i,s}$ is the Stokes radius of the solute i and r_p the pore radius). They depend not only on λ_i but

Nanofiltration (Transport Phenomena),

Fig. 1 Concentration polarization phenomenon. c_i^{feed} , concentration of solute i in the feed solution; c_i^{perm} , concentration of solute i in the permeate; c_i^m , concentration of solute i at the membrane surface; J_V , permeate volume flux



also on the radial position within the pore. However, the effect of the finite pore size on both diffusion and convection can be quite accurately estimated using the values of $K_{i,c}$ and $K_{i,d}$ at the pore center only (Deen 1987). Several approximate analytical expressions derived using the centerline approximation are available in the literature.

The solute molar fluxes j_i are related to the permeate volume flux J_V (based on membrane area) as follows:

$$j_i = V c_i^{\text{perm}} = \frac{J_V c_i^{\text{perm}}}{A_k} \quad (2)$$

where c_i^{perm} is the bulk concentration of solute i in the permeate and A_k the membrane porosity.

It should be noted that, as with any membrane separation process, the separation of solutes is also influenced by transport through the polarization layer, which is caused by solute accumulation in the boundary layer adjacent to the membrane. The pressure-driven fluid flow through a selective membrane convectively transports solute toward the surface membrane. The partially or totally retained solutes accumulate at the membrane surface generating a concentration gradient, which induces a diffusive flux of solute from the membrane surface toward the feed bulk (Fig. 1). The solute builds up at the membrane surface until the equilibrium between diffusive and convective solute fluxes is attained. The concentration in the membrane boundary layer is critical for both fouling and retention. The importance of the

concentration polarization phenomenon increases with the permeation flux because more species are then brought near the membrane surface under the action of convective flow. Similarly, an increase in the concentration of the feed solution leads to a more important polarization. Concentration polarization is generally considered as a reversible process that can be controlled by velocity adjustment, pulsation, or electric field.

Cross-References

- Donnan Effect
- Electrical Double Layer
- Fouling in Membranes
- Nanofiltration

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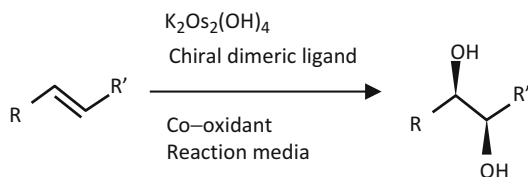
Nanofiltration for Reuse of Sharpless Catalytic Systems

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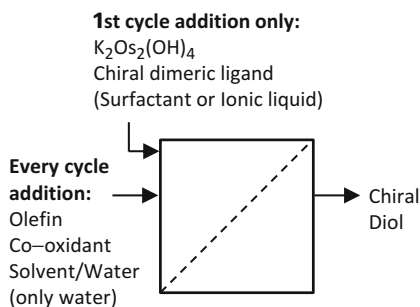
Nanofiltration for reuse of Sharpless catalytic systems combines reaction and separation in a

single vessel, allowing successive reaction and filtration steps, to recycle the catalytic system in successive batches with isolation of the chiral product on the permeated solution. The Sharpless catalysis is a robust strategy for production of chiral 1,2-diols from olefins at high yields and enantiomer excesses, using a catalytic system based on OsO_4 or $\text{K}_2\text{OsO}_2(\text{OH})_4$ salt and a chiral dimeric ligand (Bolm et al. 2000; Kolb et al. 1994). Chiral ligands used are based on a *cinchona* alkaloid (dihydroquinidine or dihydroquinine) with phthalazina, pyrimidine, or indoline groups. The reaction requires a co-oxidant, which can be organic or inorganic, such as *N*-methylmorpholine-*N*-oxide (NMO) or $\text{K}_3\text{Fe}(\text{CN})_6$, respectively. The reaction media is conventionally an aqueous/organic (50 v/v% solvent) mixture with *tert*-butanol, methyl *tert*-butyl ether, or acetone. The feasibility of Sharpless reaction was also attained for a range of seven different olefins on the absence of organic solvent, using an aqueous system that includes a surfactant, such as sodium dodecyl sulfate and sodium cholate, or an ionic liquid such as hexadecyltrimethylammonium bromide (Branco and Afonso 2002; Branco et al. 2008). Moreover, the use of aqueous/surfactant or ionic liquid systems avoids the continuous gradual slow addition, required to obtain high enantiomer excesses in the aqueous/organic system. Widespread industrial application of the Sharpless system has been restricted by the high cost of the catalyst and toxicity of the osmium species. Aqueous and **organic solvent nanofiltration** had been assayed to isolate chiral product and recycle the osmium salt and chiral ligand hydroquinidine 1,4-phthalazinediyl diether (molecular weights, MW, of 368 Da and 779 Da, respectively) (Branco et al. 2008; Ferreira et al. 2007) into successive reactions. NMO with a molecular weight of 135 Da was used as co-oxidant for both aqueous/organic and aqueous/surfactant systems. Starmem120, a polyimide membrane with nominal **molecular weight cut-off** (MWCO) of 200 Da, was used for the aqueous/organic system, composed of a water/acetone (25 v% acetone) mixture, with a lower water content than in the conventional Sharpless system, to improve solvent mixture flux through the



Nanofiltration for Reuse of Sharpless Catalytic Systems, Fig. 1 Reaction scheme for asymmetric dihydroxylation of olefins

membrane (Ferreira et al. 2007). On the other hand, a ► **polyamide membrane**, Desal DK, with a MWCO of about 250 Da, was used in the aqueous/surfactant system to retain both catalytic system and sodium cholate (Mw 460.6 g.mol⁻¹), the surfactant used (Branco et al. 2008). In both systems, each reaction-membrane filtration cycle included a first reaction step at atmospheric pressure, without permeation, and a second ► **nanofiltration** step in which a pressure of 10–20 bar was applied as driving force to promote solution permeation through the membrane. The next cycle started by making up the feed volume with addition of solvent/water or only water in the water/surfactant system. Different steady states, concerning product concentration in the vessel, can be reached according with concentration factors (i.e., the ratio of initial per final volume) used. Product concentration can be important in the final process yield due to reaction inhibition by the product. ► **Diafiltration** strategies with feeding of additional solvent/water (or water alone) can also be employed in the ► **nanofiltration** step to reach lower product concentrations in the vessel and recovery higher product amounts in the permeate. However, for higher diavolumes, when catalyst and surfactant have rejections lower than 100 %, losses of the catalytic system into the permeate can become significant. Moreover isolation of the more diluted product from permeate is more challenging. Overall, the application of nanofiltration for reuse of the osmium catalytic system as the potential to improve turn over numbers (TON), (i.e., total product obtained by catalyst used) with beneficial impact on Sharpless reaction economics and osmium contamination of the product (Figs. 1 and 2).



Nanofiltration for Reuse of Sharpless Catalytic Systems, Fig. 2 Scheme of nanofiltration-reaction successive cycles

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Nanofiltration in Textile Industry

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The wastewaters generated from the textile industry are among the most polluting of all the industrial sectors and have been considered as a

significant environmental problem for several decades (Avlonitis et al. 2008). Dyes by very nature are chemically robust, are often toxic, and are typically in the molecular weight range of a few hundred Daltons. Most developed nations recognize the impact and toxicity of dyes that are released into the environment and have legislation in place to prevent such discharges necessitating the cleanup of such waste streams. There is great variation in the chemical nature of textile discharge which can vary dramatically depending on the type of product produced and chemicals involved in the particular textile factory. Due to the very stable nature of dyes, traditional technologies such as adsorption and physiochemical methods, photocatalysis and oxidative methods, and microbiological and enzymatic decomposition are of relatively little use in the recovery or destruction of dyehouse effluent. However, nanofiltration membranes have the potential to offer an improved separation and several cost advantages over these more traditional techniques, and various works have reported the use of NF membranes for dye separations either for wastewater treatment (Nataraj et al. 2009; Mo et al. 2008) or process applications (Levenstein et al. 1996). In most cases, the dye wastewater also contains residual salt from the manufacturing process. The removal of dye should be high, but not necessarily complete, and the fate of the salt is of less importance. A review of NF processes in the textile industries has been compiled by Lau and Ismail (2009) and has indicated that most commercial membranes either achieve a maximum separation of the dye or high membrane flux. The desirable ideal membrane should exhibit both characteristics. The ideal separation when considering nanofiltration membranes should utilize both the steric and Donnan separation effect. For example, if one considers the separation of a waste containing a mixture of both Clayton Yellow (MW = 696 Da) and methyl orange (MW = 327 Da), then a neutral membrane with a MWCO of ~500 could potentially achieve this separation based on the steric effect. If one considers the separation of methyl orange (MW = 327 Da, negatively charged) from methylene blue (MW = 320 Da, positively charged),

then a negatively charged 600 MWCO membrane would potentially retain the methyl orange (Su et al. 2004) and a similar positively charged membrane would retain methylene blue (Cheng et al. 2012). In each of these cases, the resulting separation would most likely require a diafiltration process to achieve high purity dyes. In the case where the desired dye is in the permeate stream, then a reverse osmosis process to reconcentrate the dye may be required prior to any recycle. Similarly, where high salt levels exist in the dyehouse effluent, the same diafiltration process may be employed to separate the dye from the salt potentially facilitating the recycle of both materials. In all cases, water recovery and recycle from the effluent streams may be achieved using nanofiltration (or in some cases reverse osmosis) which can lead to a significant operational cost saving.

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Nanofiltration Membranes

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Synonyms

NF Membranes

General View

Nanofiltration membrane is a pressure-driven membrane, with a nominal molecular weight cut-off (molecular weight of solute that is 90 % rejected by the membrane) ranging from 200 to 1000 Da, pore size of around 0.2–2.0 nm, and operating pressures of 70–200 psi (5–15 bar) (Schäfer et al. 2002). Although a common belief indicates that NF and RO membranes do not possess distinct pores, as in ultrafiltration (UF) and microfiltration (MF) membranes, recent studies using atomic force microscopy suggest that pores of NF membranes can be viewed (Daraei et al. 2013).

In the early stages, nanofiltration membranes were named as ultralow-pressure reverse osmosis (RO), charged ultrafiltration, loose RO, tight UF, lower rejecting or open RO, and selective RO membranes (Schäfer et al. 2002).

The nanofiltration membrane was defined in 1987 by Simpson et al. (1987) in the first publication with the title of nanofiltration as: “These charged membranes possess properties lying between those of reverse osmosis and ultrafiltration membranes. Molecules with a molecular mass greater than 300–400 Da, e.g., glucose, are rejected and inorganic ions are selectively excluded according to their charge densities.”

Nanofiltration membrane is primarily used to separate low molecular weight organics and

multivalent salts from monovalent salts and water. They provide 50–90 % salt rejection at low-pressure operation. This reduces energy consumption and significantly lowers installation and operating costs.

Nanofiltration membranes provide specific advantages over conventional membranes. They exhibit higher flux at lower pressures versus reverse osmosis and improved rejection compared to ultrafiltration membranes.

Applications

In the early stages, nanofiltration membranes were employed in softening and natural organic matter removal for drinking water treatment. Nanofiltration membranes were grown rapidly due to unique capability of fractionating ionic and low molecular weight organic species. This type of membrane has been an important separation and purification technique in not only aqueous feeds such as water treatment and pharmaceutical purification but also emerging applications in organic solvent and ionic liquid-based separations. Currently, the application of nanofiltration membrane is growing in chemical, desalination, concentration and purification, paper, whey, semiconductor, textile, and leather industries and recycling of valuable homogenous catalysts.

The removal of heavy metals from wastewater, removal of pesticides from groundwater, recycling wastewater in laundries, water softening, and nitrate removal are the outstanding applications of nanofiltration membranes.

Nanofiltration in water treatment “bridges” a gap between ultrafiltration and reverse osmosis membranes. There are many applications where a 75 % rate of salt rejection is preferable to 99 %, especially when it is achieved using only half of the energy. Typically reverse osmosis membrane with less than 99 % sodium chloride removal is considered inferior. In the case of NF, there is a “place” for any membrane with NaCl rejection rate of 40 % or more.

Mechanisms

The major separation mechanisms of nanofiltration membrane involve a steric (size exclusion) effect and an electrostatic interaction (Donnan exclusion) between the membrane and an external solution. Charged membrane with a “loose” polymer structure enables separation of ions enhanced by Donnan exclusion. For nanofiltration membrane, both surface charge and sieving mechanisms affect the rejection of solutes, which are usually characterized by high retention of divalent ions, low rejection of monovalent ions, and high flux.

Size exclusion is a simplified retention model that is based on physical size of a contaminant. Usually the solutes larger than the pore size of the membranes are retained. This model is based on the sieving phenomenon. However, one should consider that the membranes neither have uniform pores nor the solutes have uniform size. The molecules are flexible in size and shape as a function of stress and solution chemistry. Moreover, trace contaminants may interact with other molecules or membrane polymer (via hydrogen bonding or hydrophobic interaction). This influences the retention.

Charge interaction is another model describing the transport of organic electrolyte across NF membrane. This electrostatic and steric-hindrance model combines space charge and steric hindrance. Based on this model, solute retention is a function of the ratio of charge density of the membrane to ionic concentration of the solvent and proportion of solute dimension in the solvent to pore size of the membrane. As a result, it is expected that retention of trace organics is influenced by solution chemistry such as pH and ionic strength.

Some trace organics may possess a negative or positive charge when the molecules dissociate at high or low pH. Negatively charged species often experience higher retention compared to uncharged molecules with the same size. This can be attributed to the electrostatic repulsion between the molecules and the negative

functional groups of the membrane. However, positively charged organics are poorly retained by the negative membranes.

The pH value of the feed solution may affect the membrane characteristics and the retention property. The most significant one is the membrane surface charge density which is often measured as zeta potential. In general, zeta potential of the membrane surface is changed from a positive to a negative value as the solution pH is increased. Subsequently, electrostatic interaction between an ionic compound and the membrane surface is varied according to the solution pH.

Adsorption of materials to the membrane surface or pores is another substantial aspect of contaminant removal using nanofiltration membranes. In fact, adsorption is recognized as the first step in the transport mechanism of water and in some cases solutes across the membrane in the well-known sorption-diffusion model. The adsorption is influenced by the charges of the molecules and membrane. This may enhance attraction or repulsion. Although adsorption contributes to initial high rejection, lower retention is often observed when the membrane has been gradually saturated.

Membrane Preparation and Modification

Most commercial nanofiltration membranes are fabricated from organic polymers. However, inorganic membranes composed of metal oxides are developing due to higher durability in numerous applications. The main goal in membrane preparation is to control membrane structure to properly affect the membrane performance.

The nanofiltration membranes may be manufactured using the conventional techniques including the well-known phase inversion and interfacial polymerization approaches. However, the preparation of nanofiltration membranes with improved properties by new materials or advanced modification methods for existing membranes is a valuable and practical technique.

A potential approach to develop new NF membranes is to modify UF and RO membranes via various procedures.

There are numerous modification methods that improve the performance of nanofiltration membrane. Generally, surface modification of membranes by functionalization methods (coating, self-assembly, chemical treatment, plasma treatment, graft polymerization, molecular imprinting, and enzyme immobilization) and nanofiller embedment are the practical ways to modify polymeric membranes in general and nanofiltration membrane in particular (Zhao et al. 2013).

Presently, most nanofiltration membranes are assembled in spiral-wound configuration using thin-film composite flat-sheet membranes.

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Nanotechnology Membrane

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Over the last decade, nanotechnology has rapidly evolved from an academic research to commercial reality. The concept of nanotechnology led to the development of innovative nanotechnology-

based membranes that surpass the state-of-the-art performance and enable new functionality such as high permselectivity, catalytic reactivity, and fouling resistance. Nanotechnology is used to enhance performance of traditional ceramic and polymeric membrane materials through various strategies (Pendergast and Hoek 2011). Nanotechnology membranes include:

- Zeolite and catalytic nanoparticle-coated ceramic membranes
- Hybrid inorganic-organic nanocomposites membranes
- Bio-inspired nanotechnology membranes
 - Bio-hybrid immobilized enzyme membranes
 - Bio-hybrid magnetic-responsive membranes
 - Aquaporin membranes
 - Vertically aligned nanotube membranes
 - Isoporous block copolymer membranes

Hybrid Inorganic-Organic Nanocomposite Membranes

Mixed matrix membranes present the synergistic advantage of both the low cost and ease of fabrication of organic polymeric membranes and mechanical strength and functional properties of inorganic materials (Dong et al. 2013). The concept was first introduced in the 1990s by Zimmerman et al., as a strategy to overcome the limitations of polymeric membranes for gas separation. The most commonly exploited inorganic fillers are alumina, carbon nanotubes, iron-palladium particles, silica, and titania, which are embedded within the polymeric matrix. The particle size covers broader ranges from 0.5 to 300 nm, while the general composition ranges from 0.01 to 40 wt.% (Pendergast and Hoek 2011). Generally, inclusion of the inorganic particle imparts change in the polymeric membrane surface property (hydrophilicity/hydrophobicity, roughness, increased or decreased water permeability and selectivity depending on the type, size, and weight fraction of the inorganic particle, improved thermal and mechanical stability, as well as enhanced antifouling property).

In addition to microparticles, nanoparticles have been added to polymeric membranes, e.g., the inclusions to the thin films of thin-film composite (TFC) reverse osmosis membrane have been of great interest to impart the properties of the nanomaterials. Embedding smaller nanoparticles increases permeability more by increasing the characteristic pore size. One of the main reasons attributing to the enhanced permeability of the TFC membranes with embedded nanoparticles is the presence of limited cross-linking than pure polyamide TFC counterparts. Overall, the addition of nanoparticles can be tailored to particular membrane applications with the selection of nanoparticle size, shape, and type. Furthermore, inclusion of the nanoparticles such as silver in the TFC could inhibit biofouling growth due to the antimicrobial property of nanosilver (Basri et al. 2010).

Nevertheless, improved permselectivity through inclusion of nanoparticle to the TFC may not be a general fact. It is theoretically predicted that the permeability of TFC, which have impermeable nanoparticles like titania, reduces, while those containing permeable nanoparticles like SOD-zeolite increases. A nanoparticle with higher water permeability relative to the polymer matrix can increase the permeability of the resulting nanocomposite membrane, while impermeable nanoparticles can only reduce the water permeability of a membrane because they reduce the area available for permeation through the polymer film. The only time impermeable particle can enhance permeability is when they cause defect in the thin-film layer which also compromises their solute rejection capacity (Pendergast and Hoek 2011).

For the impermeable particles, even with the presence of loss in permeability, inclusion of the nanofillers could be desirable to induce hydrophilic or antimicrobial properties that significantly reduce membrane fouling. In addition to performance, one also has to take the cost of the nanofillers into consideration for practical application. For instance, antimicrobial and zeolite nanoparticles are expensive, yet zeolite nanofillers can bring about a considerable flux improvement at extremely low loadings such that the cost increase may be minimal.

Other interesting features one can induce by inclusion of nanofillers into polymeric membranes are stimuli-responsive properties. One of the main strategies that follows the research on stimuli-responsive organic-inorganic (O/I) hybrid membranes is the incorporation of superparamagnetic nanoparticles (NPs^{SP}). It is an emerging field that holds numerous unexplored interesting avenues (Daraei et al. 2013; Sanchez et al. 2011). It leads to stimuli-responsive “smart” polymeric membrane with properties that can be modulated in a reversible manner. For example, recently magnetic-responsive micro-mixing nanofiltration membrane is developed. The membrane was prepared by grafting magnetic-responsive nanolayers consisting of hydrophilic poly(2-hydroxyethyl methacrylate) (polyHEMA) flexible polymer chains with NP^{SP} attached to the chain ends. The chain oscillates in an oscillating magnetic field, induced mixing at the membrane-fluid interface that maximized the disruption of concentration polarization layer (Himstedt et al. 2011).

NP^{SP} has also been used as inorganic nanofillers in a PVDF membrane to impart desired surface functionality (Huang et al. 2012). The hybrid membrane has controlled porosity, texture, and chemical composition that can provide real prospect to an efficient membrane filtration. The presence of the NP^{SP} also induces magnetic property in the membrane that can be controlled by an external magnetic field through remote on-off switches (Daraei et al. 2013; Thevenot et al. 2013). This responsive behavior, for example, is useful to manipulate the deposition of magnetic nanoparticle on the membrane surface to prevent direct membrane-foulant interaction (Gebreyohannes et al. 2015). In addition to inducing magnetic properties, inclusion of the NP^{SP} is reported to enhance the membranes’ hydrophilicity, mechanical strength, compaction resistance, improved permselectivity, and antifouling property (Daraei et al. 2013; Huang et al. 2012). Therefore, these membranes have broad function ranging from environmental remediation to smart product manufacturing. Particularly, the synergistic antifouling property and improved permselectivity give the membrane a big prospect to be utilized in water purification. NP^{SP}-coated

membranes, for example, have been used for effective removal of natural organic matter (Yao et al. 2009), arsenic (Sabbatini et al. 2010), and copper (Daraei et al. 2012) during water treatment.

Bioinspired Nanotechnology Membranes

Biomimetic nanostructured membranes are formed either through directly embedding biomolecule into synthetic materials or by using functional molecules to modify synthetic materials to impart specific biological property. These hybrid biomimetic membranes combine the accurate structure of a biological pore with the durability, robustness, and the possibility to control the pore size and shape of solid-state nanopore membrane (Shen et al. 2014).

Biohybrid Magnetic-Responsive Membranes

Superparamagnetic nanoparticles (NPs^{SP}) are most often superparamagnetic iron oxide with zero memory of their magnetic property in the absence of an external magnetic field (Yeon et al. 2009). Polymer coatings and the introduction of various surface functional groups facilitate the anchorage of biomolecules on the surface of these particles (Miguel-Sancho et al. 2012; Brullot et al. 2012; Xiao-Ming and Wainer 1993). The resulting bionanocomposites represent an important material with a versatile application in the biotechnology, fine chemicals, drug delivery, cell transplantation, or cell immobilization. These nano-sized particles exhibit biocompatibility, high surface-to-volume ratio which makes them a good candidate for enzyme immobilization to make biohybrids. The high surface-to-volume ratio assists with higher enzyme loading capacity and enhanced mass transfer efficiency. Hence this material with its excellent mechanical, optical, electrical, ionic, and catalytic properties is a good candidate to reversibly immobilize enzyme on the surface of a polymeric membrane to mimic hybrid protein-polymer biomimetic membranes.

Alternative to direct integration of the enzyme within the polymer matrix, stimulus-responsive

programmable layers on membrane can be formed through the attraction of NP^{SP} through reversible magnetic force. These biomimetic smart layers will enable development of adaptive enzyme membrane reactors. For instance, once an enzyme is immobilized on NP^{SP}, they can be easily dispersed in a reaction medium in the absence of an external magnetic field. However, by applying an external magnetic field, it is possible to relocate the bionanocomposites toward the surface of a membrane using an external magnetic field. The method is promising to resolve pertinent issues related to the direct integration of enzyme within the polymeric matrix. Overall, tuning reversible enzyme immobilization using NP^{SP} helps in:

1. Easy recovery, recycling, and removal of immobilized enzyme
2. Formation of dynamic layer between membrane and feed preventing membrane-pollutant interaction
3. Activation of the monolayer with biocatalyst to achieve biocatalysis at the membrane-solution interface
4. Easy regeneration of membrane whenever the membrane is oversaturated with substrate

This approach has recently been demonstrated to form an enzyme membrane reactor (Gebreyohannes et al. 2015). The method is novel for it has used NP^{SP} as a carrier to anchorage various enzymes as well as nanofiller to form magnetic-responsive hybrid membrane. When an external magnetic field has been applied to the system, the magnetic-responsive polymeric membrane gets magnetized. Subsequently, the NP^{SP} with the immobilized enzyme was dispersed in the upper stream. These particles were then attracted toward the surface of the membrane. The magnetic-responsive membrane acts as magnetic field actuators that eventually help with uniform dispersion of the NP^{SP} on the surface of the membrane. Hence it has potentially mimicked the micro-nanoarchitecture of the direct integration of enzyme into the membrane.

The method has shown an interesting performance when it was applied to treat a feed rich in polysaccharides. After depositing 1–2 g/m² of

pectinase activated NP^{SP} with an average diameter of 8 nm, 40 % to 100 % reduction in the pressure required to keep flux constant at 17 L/m² h was observed. Moreover, thanks to the easy recycling of enzyme, both membrane and immobilized enzyme were used over several cycles, adding a considerably extended lifetime to the membrane as well as the enzyme (Gebreyohannes et al. 2015).

Modulating reversible enzyme immobilization through combinatorial stimulus-responsive enzyme immobilization technique holds a great potential in bioseparations, antifouling surfaces, and creating self-cleaning membranes. Hence, the future innovations on the basis of stimulus-responsive enzyme immobilization holds a bigger prospect to “reengineer” membrane biocatalysis that will lead to the design of more complex membrane systems that are capable of mimicking the nature.

Aquaporin Membranes

Aquaporins are the protein channels that control water flux across biological membranes. Water movement in aquaporins is mediated by selective, rapid diffusion caused by osmotic gradients (Agre 2006; Meinild et al. 1998). According to Zhu et al. (nd), the two major factors that control water transport are:

- (a) Osmotic permeability: molecular movement due to concentration differences resulting in net mass transfer
- (b) Diffusion permeability: random movement of molecules with no net mass transfer

In the first case, the water molecules transport in a single file through a narrow aquaporin channel, while in the second case, permeation occurs due to the movement of two molecules between opposite pools. Hence, the ratio of the osmotic permeability to diffusion permeability is the number of effective steps a water molecule shall move in order to permeate through a channel. Since aquaporin channels have high water selectivity, a membrane with 75 % aquaporin coverage is predicted to have an order of magnitude higher water permeability compared to commercial seawater RO membranes (Kaufman et al. 2010).

There already are interesting research activities on the inclusion of aquaporins in polymeric membranes. For instance, the use of aquaporin-Z from *E. coli* bacterial cells used to form a protein-polymer membrane exhibited an order of magnitude higher water permeability as compared to a counterpure polymeric membrane. However, practical application of these proteins is highly limited by lack of large quantities of protein production. Nevertheless, with a continued research and effort, techniques to simplify the fabrication and production of mechanically sound membranes aquaporin-based biomimetic membranes are inevitable.

Vertically Aligned Carbon Nanotubes

Carbon nanotubes (CNTs) exhibit the fast mass transfer resemblance to aquaporin water channels in which water transport is two to five times higher than theoretically predicted by Hagen-Poiseuille equation (Holt et al. 2006). Molecular dynamic simulation studies attributed this outstanding flow rate to atomic smoothness and molecular ordering. In particular, water molecules permeate through the CNTs in a one-dimensional single file resulting in very small driving force use. Moreover, CNT-based membrane represents excellent mechanical properties that impart longer lifetime than conventional membrane materials.

The most commonly utilized mechanism used to produce uniformly aligned nanotube arrays is chemical vapor deposition (CVD). The CNTs are adapted by fixing surface functional groups to mimic aquaporin structure or by CVD and a simultaneous solid-state reaction (Holt et al. 2006). The pore densities of the CNTs made by fixing negative surface functional groups are as high as $0.25 \times 10^{12}/\text{cm}^2$ while representing three order of magnitude higher water flux relative to what is predicted theoretically. However, CNTs' alignment via CVD has a number of limitations such as its costliness, sensitivity, and difficulty for large-scale application. Alternative to CVD, magnetic alignment, self-assembly, and passing single-walled CNT suspensions through polymeric filters are approaches to form CNT-aligned membranes.

Although CNT mimicked biological aquaporin channels with a material producible in large

amount, no large-scale CNT-aligned membranes have been produced yet. However, one can resolve these challenges similar to the challenges faced by reverse osmosis membranes 50 years ago when performance improvements lead to the practical necessity of CNT-aligned membrane application.

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Natural Gas Sweetening

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Introduction

Though raw natural gas is mainly composed of methane (generally from 75 % to 90 %), it also contains undesired components such as acid

gaseous impurities such as carbon dioxide or hydrogen sulfide that should be removed in order to prevent pipeline corrosion.

Permeation Membrane-Based CO₂ Removal

Gas permeation constitutes the latest carbon dioxide extraction technology applied to natural gas treatment. Membranes offer several strong advantages over conventional solvent columns: compacity (which makes membranes particularly well-suited for offshore operations (Cooley and Dethloff 1985)), low investment costs, low maintenance costs, and at least with single-stage configurations that do not operate compressors. The current level of commercial membranes CO₂/CH₄ selectivity is comprised between 12 and 25 in field conditions (Baker 2002; Roman et al. 2001; White et al. 1995; Baker and Lokhandwala 2008).

Several studies have been carried out since the adoption of membranes by natural gas operators, aiming at comparing membrane-based carbon dioxide removal operations with conventional absorption operations. Several trends can be issued from these studies, depending on the various considered gas treatment scenarios:

- Moderate natural gas flows (lower than 25,000–30,000 Nm³/h (Chapel and Mariz 1999; McKee et al. 1991)) containing high carbon dioxide concentrations: it appears that membranes are more profitable than absorption processes. In 1995, it was shown that commercial permeation membranes were more competitive than DEA/MDEA-based absorption when the carbon dioxide content was higher than 20 % (Meyer and Gamez 1995). Another study realized by Kellogg & Co. sets this limit at approximately 16 % for a gas price of 1.5 USD/MMBtu (McKee et al. 1991).
- High natural gas flows with low carbon dioxide concentrations: absorption processes prove to be more profitable than gas permeation modules.
- High natural gas flows combined with high carbon dioxide content: an association of

membranes and absorption seems to be the most profitable option (McKee et al. 1991). Membrane modules, located before the absorption column, carry out a bulk removal of carbon dioxide, while the absorption columns allow the final polishing of the natural gas.

Permeation Membrane-Based Hydrogen Sulfide Removal

Three main types of polymer membrane have been only tested at lab scale or pilot scale in order to remove hydrogen sulfide from natural gas.

Membranes Based on Rubbery Polymer Selective Layers

This type of polymer materials generally offer very high permeability values for low molecular weight components. The selectivity of this type of polymer is then essentially based on the affinity (i.e., the sorption coefficient) difference between several components to be separated. In the literature, three main polymer families can be identified:

- Apolar rubbery polymers, such as silicones (PDMS and PTMSP). As a general rule, the H₂S/CH₄ selectivity of these materials is rather modest, as methane diffuses more rapidly than hydrogen sulfide (Merkel et al. 2001).
- Apolar rubbery polymers impregnated with polar solvents: two patents have been issued by UOP in the mid-1980s about the use of PEG- or glycerol-impregnated silicone membranes. The addition of polar solvent, which displays a high affinity for hydrogen sulfide, leads to a very significant increase of the selectivity of these membrane materials toward hydrogen sulfide (Kulprathipanja and Sudhir 1985; Kulprathipanja 1985).
- Polar rubbery polymers: these types of polymer have mainly been studied by academic teams and display high values of H₂S/CH₄ selectivities associated with high H₂S permeabilities. To the authors' knowledge, though, those materials have not been studied on larger scale than at lab (Chatterjee et al. 1997; Orme and Stewart 2005).

Membranes with a Selective Layer Made of Block Polymers

This type of membrane materials has been principally studied by *MTR Inc.* which has developed commercial spiral-wound membranes with a selective layer made of various polyether block amides (commercialized under the trademark PEBAX[®] by *Arkema*). Tests under industrial conditions were conducted on production facilities operated by Shell and located in West Texas (Amo et al. 1998). It was shown that the PEBAX[®]-based membranes/sulfatreat process association was leading to significant operation costs (from 20 % to 40 %) over amine process alone for flow gases containing few percents of H₂S and lower than 140,000 Nm³/h while a PEBAX[®] membrane/amine coupling was more valuable than a stand-alone amine process for gas flows containing more than 5 % H₂S and higher than 23,000 Nm³/h.

Membranes with a Selective Layer Made of Glassy Polymers

Those stiff polymeric materials, used mainly for commercial carbon dioxide removal applications (polyimides, cellulose acetate, polysulfones), have their selectivity mainly based on molecular sieving effects. Despite their affinity for polar compounds (those membranes are also recommended by membrane manufacturers for gas dehydration applications), it appears that those membrane materials have rather low H₂S/CH₄ selectivities (Hao et al. 2008; Bhide et al. 1998). This can be mainly attributed to the fact that the kinetic diameters of hydrogen sulfide and methane are rather close, resulting in close values of their respective diffusion coefficients through glassy polymer-based selective layers.

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Natural Organic Matter (NOM)

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Natural organic matter (NOM) is an organic material from environmental origin and produced by biodegradation of organic substances (plants, etc.).

NOM gives surface waters a brownish color and is a problem in drinking water supply, not because of its toxicity but because some of its components can react with chlorine used as disinfectant. The reaction by-products include trihalomethane, haloacetic acids, chlorophenols, etc. which are potentially carcinogenic. The NOM components are known as trihalomethane precursors (THMPs), and it is recognized that their removal prior to disinfection is important for public health. Membrane technology is frequently used for treatment to remove NOM from surface waters (see ► [Natural Organic Matter, Removal and Fouling of](#)).

Natural organic matter (NOM) has a broad spectrum of molecular weights and size distributions, functional groups, and substructures. The term NOM covers the particulate colloids (POM), “dissolved” colloids, and macromolecules or dissolved organic matter (DOM) and the humics. Since NOM is from environmental origin, its composition is highly variable both spatially and temporally. One of the major groups in NOM is humic substances (HS), which include a complex mixture of organic compounds such as humic acids (HA), fulvic acids (FA), and other hydrophilic compounds. Typically, humic substances have molecular weights from a few hundreds to approximately 100,000 Da. They contain both aromatic and aliphatic components with carboxylic and phenolic groups attached to the aromatic rings. As a result, humic substances can be negatively charged as well as having hydrophobic and hydrophilic components. The humic fraction also has neutral components. The charge character is important as it influences interactions with other pollutant species and the treatment process equipment (such as membrane surfaces).

The complexity of NOM makes characterization difficult. A review of methods can be found in Leenheer and Croue 2003. Recently NOM characterization has involved size exclusion chromatography, combined with UV and online DOC and organic nitrogen detection, in a system called “liquid chromatography-organic carbon detection-organic nitrogen detection” (LC-OCD-OND) (Huber 2014). This instrument provides a molecular weight distribution and also identifies components (in descending size) as biopolymers, humics,

building blocks, low MWt acids and humics, and neutrals. This measurement technique is now widely used in membrane applications to water and wastewater.

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Natural Organic Matter, Removal and Fouling of

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Natural organic matter (NOM) is present in surface waters and its removal prior to disinfection is important to avoid formation of potentially carcinogenic trihalomethanes (see “► [Natural Organic Matter \(NOM\)](#)”). With a size range from colloidal to a few hundred Daltons the NOM species are well suited to removal by membranes, including removal of trihalomethane precursors (THMPs). However, some of the components of NOM are potential membrane foulants, as discussed below.

Most typically, NOM removal involves microporous membranes (micro- or ultrafiltration), often in combination with a coagulant (ferri-salts, polyaluminium chloride, etc). The hybrid processes, combining membranes with chemical addition, give improved removals as seen in Table 1. The hybrid processes also provide

Natural Organic Matter, Removal and Fouling of,
Table 1 Typical removals of NOM by membranes

Process	TOC/DOC	THMP
	Removal (%)	Removal (%)
Microfiltration	10–40	15–20
MF + chemical	~80	~60
Ultrafiltration	~50	~40
UF+ chemical	~90	~80
Nanofiltration	90–99	90–99

better control of membrane fouling (see below). The disadvantage is the disposal of the waste sludge solids. Nanofiltration (NF), with pores in the 5–2 nm size range, is capable of high removals of NOM and is used extensively in Norway and Scotland, particularly in remote areas where chemical dosing would be troublesome. This advantage of NF may be offset by higher pressures and energy costs in some applications.

NOM fouling of membranes is complex with many influencing factors, including the variable nature of the raw water. It should be noted that no one single component of NOM has been identified as the major cause for membrane fouling and there are conflicting views in the literature. However, some components are clearly implicated. The mechanisms of UF membrane fouling have been shown to be cake formation, pore restriction by adsorption, and pore plugging (see “► [Irreversible Fouling](#)”). Both reversible and irreversible fouling have been found in the membrane treatment of surface waters. Thus, a fraction of NOM with molecular sizes smaller than the membrane pores may adsorb and reduce the pore cross-sectional area for permeation and larger fractions may plug pore entrances or contribute to cake formation.

The hydrophobicity/hydrophilicity of NOM has been found to be a factor influencing membrane fouling in natural water treatment. There is evidence that the hydrophobic components in NOM tend to be responsible for the fouling of hydrophobic membranes due to hydrophobic interactions. However, there are contrary views. In an Australian study, NOM was isolated into four fractions: hydrophilic neutral, hydrophobic acids, transphilic acids, and hydrophilic charged. The

order of the fouling potential of the individual components during MF with PVDF membranes was hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. However, it may be that the hydrophilic neutral fraction exhibited the greatest fouling potential because of its size (>30 kD) relative to the membrane pore size. The components of NOM can also be fractionated into the following four fractions by pyrolysis-GC/MS: polysaccharides, proteins, polyhydroxy-aromatics, and amino sugars. It has been found that the fouling potential could be ranked in the order of polyhydroxy-aromatics > proteins > polysaccharides and amino sugars. The polyhydroxy aromatics were thought to be the main foulants for negatively charged NF membrane surfaces, and are probably hydrophobic acids with phenolic groups, exhibiting no negative charge at a neutral pH. However, this could change in the presence of calcium, and similar divalent cations, that appear to exacerbate NF fouling by NOM due to binding between the negative membranes and negative components of the NOM.

Controlling NOM fouling can significantly reduce the cost of membrane water treatment, extend membrane life, and reduce energy demand. Techniques developed to minimize NOM fouling include hybrid membrane processes, pretreatment to reduce the NOM in the raw water, optimization of hydrodynamic parameters, careful membrane selection, and cleaning of the membrane system.

Hybrid membrane processes involve the combination of coagulation/flocculation, or sorbents, such as powdered activated carbon (PAC), heated iron oxide particles (HIOPs), or an ion-exchange resin (such as MIEX[®]) with membrane processes. MIEX[®] is an anion-exchange resin capable of removing relatively low molecular weight negative organics from NOM. It has been shown that using MIEX[®] to remove organics leads to very low fouling of a UF membrane which is hydrophilic and positively charged. The performance was particularly enhanced when calcium was removed. Pretreatment strategies include biologically activated carbon, where a bed of granular carbon with developed biofilms treats the feed water and reduces the biodegradable components of NOM.

Hydrophilic membranes have been found to be less prone to fouling than hydrophobic membranes when treating natural water containing NOM. Unfortunately, most commercially available UF and MF membranes are relatively hydrophobic materials with low surface energies such as polypropylene, polysulfone, polyethersulfone, and polyvinylidene fluoride. Some membranes (such as PVDF) can be rendered more hydrophilic by blending or surface treatment. A recent development involves the use of ceramic UF membranes with ozone pretreatment to oxidize NOM components. This method appears to limit fouling, even at relatively high fluxes.

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NaY Membrane for Gas and Vapor Separation

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Zeolite membranes owing to their crystalline structure and their pore size at molecular scale allow the continuous separation of gas and liquid mixtures on the basis of diverse molecular size and shape (e.g., isomers azeotropic mixtures) and also on the basis of different adsorption properties (Algieri et al. 2009). High attention was focused on NaY (FAU) zeolite membranes for the separation of CO₂ from light gases. FAU-type zeolite has pore of 0.74 nm and super-cages of 1.3 nm. The change of the Si/Al ratio during the synthesis

permits to obtain FAU zeolite with different adsorption properties, NaX (Si/Al = 1.0–1.5) and NaY (Si/Al > 1.5). NaY membranes, prepared by secondary growth method, exhibited high CO₂/N₂ separation factors (Kusakabe et al. 1997). The prepared membranes were almost defect free. The transport of the molecules took place only through the zeolite pores. The CO₂ passed easily through the zeolite pores being preferentially adsorbed on the wall of the zeolite with respect to the N₂. This behavior occurs because the CO₂ presents a quadrupole moment, while the nitrogen is a nonpolar specie. Hasegawa and coworkers (Hasegawa et al. 2001) prepared exchanged X-NaY membranes (X is K, Rb, and Cs ions) and studied their effect on CO₂/N₂ separation. The experimental results showed highest permeation selectivity with the Rb due to the high sorption selectivity with the Rb-NaY membrane. The results obtained in gas separation process at lab scale are interesting; however, the reproducibility problem during the membrane synthesis and the presence of intercrystalline defects into the zeolite layer hindered the application of these membranes at industrial level. In fact, today, their industrial application is only represented by LTA topology used for the dehydration of different organic solvents by pervaporation or vapor permeation (Morigami et al. 2001). However, LTA topology with a very high aluminum content is stable in a limited range of pH (6.5–7.5). Thus, different research groups studied the application of FAU membranes, more chemically stable than LTA membranes, in pervaporation (PV) or vapor permeation (VP) processes. NaY membranes were used in PV experiments to separate water from ethanol at 75 °C (Sato et al. 2008). Other experiments were performed with ethanol in PV and VP up to 130 °C and 570 kPa. The ethanol fluxes were linearly proportional to the driving force for VP and PV. These performances could be sufficient to use them in the actual industrial permeation processes. Recently, NaY membranes were also used to separate 1,3-propanediol from glycerol and glucose in aqueous solutions. The PV experiments at 35 °C exhibited very high separation selectivity

(1,3-propanediol/glycerol = 80; 1,3-propanediol/glucose = 2400).

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n-Butane Dehydrogenation by Membrane Reactor

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n-Butane dehydroisomerization is a one-step reaction process allowing direct conversion of n-butane to isobutene. It is an alternative to the current isobutene production process by petrochemical cracking and from butane feed (see ► [Dehydroisomerization of N-butane to Isobutene](#)) (Romanow-Garcia et al. 2007; Obenaus et al. 2005). Isobutene is an important intermediate in the petrochemical industry, used as a raw material to produce, for instance, fuel additive (ethyl *tert*-butyl and methyl *tert*-butyl ether) and rubbery materials (polybutene, isoprene). The forecast is for the worldwide demand for isobutene to increase; thus, the interest in

further improving its production is great. Membrane reactor application is an interesting strategy for such dehydrogenative-type reactions, equilibrium limited. A membrane reactor (MR), operating as an extractor, allows removing one of the reaction products from the reaction volume, shifting the equilibrium toward further product production. Moreover, an MR gives the possibility of exceeding the equilibrium constraint of traditional reactors (TRs) improving the conversion achievable and/or lowering the reaction temperature in endothermic, equilibrium-limited reactions of this type (Al-Megren et al. 2013; Marigliano et al. 2003). Yield and selectivity of reaction can be also enhanced, depleting the undesired side reaction. In addition, the MR application, combining the reaction and separation in the same unit, pursues the development and application of integrated processes, as suggested by process intensification criteria (Stankiewicz and Moulijn 2002). Reduction in the equipment number and size, improvement of the process efficiency, and, hence, a better process economy are some of the expected benefits. MRs were investigated, for instance, for the dehydrogenation of ethane, propane, and isobutane, and the authors experimentally demonstrated that conversion of these light hydrocarbons was substantially higher (Alireza et al. 2008; Abashar and Al-Rabiah 2005; Szejner and Sheintuch 2004). In all of these reactions, hydrogen is produced as a coproduct of another valuable chemical. For dehydrogenative-type reactions, H_2 -selective MRs are considered. When these reactions are carried out in an MR, the hydrogen can be removed with high selectivity from the reaction mixture and recovered at high purity directly on the permeation side, as a valuable chemical. Many types of membranes (Sanchez and Tsotsis 2002) have been investigated for this type of application.

Isobutane dehydrogenation using catalytic MRs was studied by a number of researchers (Van den Bergh et al. 2011; Yanglong et al. 2003; Babak et al. 2009).

For example, isobutane dehydrogenation has been studied using γ -alumina, zeolite MFI, palladium/silver and palladium, dense silica, and carbon molecular sieve membranes.

Using a palladium/silver composite MR, increased selectivity and yield with respect to a fixed-bed TR has been obtained (Liang and Hughes 2005). The dehydrogenation of isobutene was studied also in a carbon molecular sieve membrane, achieving 40 % conversion at 500 °C, compared with 32 % at a closed-system equilibrium (Van den Bergh et al. 2011). A thermodynamic analysis carried out on direct conversion of n-butane to isobutene in a membrane reactor, by taking into account simultaneously the chemical reaction and permeative equilibria, showed shift in equilibrium conversion as a result of selective extraction of hydrogen (Al-Megren et al. 2013). The peculiarity in the MR of the selective hydrogen removal allows exploitation of the positive effect of the reaction pressure on the hydrogen permeation and consequently on the conversion, which, on the contrary, in a TR decreases because the reaction occurs with an increase in the number of moles. An MR operating at 500 °C and 20 and 0.1 bar as reaction and equilibrium hydrogen partial pressures, respectively, reaches an equilibrium conversion seven times higher than that obtainable in a TR.

Application of membrane reactor technology to carry on hydrocarbon dehydrogenation reactions allows increasing conversion and yield of dehydrogenated product but also, producing pure hydrogen, adding value to the whole process.

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N-Butane Oxidative Dehydrogenation by Membrane Reactor

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Introduction

Butene, isobutene, and butadiene are mainly obtained from steam crackers, but the increased use of natural gas as feedstock has decreased the availability of C4 olefins. Therefore, these olefins are increasingly produced by the dehydrogenation of the corresponding alkane. Since that is an equilibrium-limited reaction, oxidative dehydrogenation has been proposed as an alternative that has raised much interest (Mamedov and

Cortés-Corberán 1995; Madeira and Portela 2002). As it happens in many selective oxidations, the undesired formation of carbon oxides (CO and CO₂) is a serious problem. As in other selective oxidations, membrane reactors have been also proposed for this reaction. Significant improvement of yield has been observed when the oxygen is distributed to a fixed bed of catalyst enclosed in a porous membrane (Téllez et al. 1997). A progressive distribution has been found to be advantageous (Ge et al. 2001). An interesting alternative is the use of CO₂ instead of O₂ as oxidant (Ge et al. 2003). The use of catalytic membrane has also been proposed (Alfonso et al. 2002). Mathematical modeling of those reactors has shown that the reactor performance agrees well with the predictions of mathematical models both for the inert membrane reactor (Téllez et al. 1999) and for the catalytic membrane reactor (Pedernera et al. 2002).

Modifications in the Reactor Configuration

This approach has been employed by several researchers with a variety of modification in the configuration:

- Pure butane in the feed to the bed entry and homogeneous oxygen distribution along the bed using a membrane.
- Butane diluted with inert gas and/or oxygen diluted with inert gas. In comparison with the previous approach, safety is increased and often the achieved selectivity is better, but the industrial application would require the separation of inert gases from the reaction products, increasing the process operation costs.
- Nonhomogeneous distribution of oxygen feed. In order to obtain a greater reaction rate at the reactor entry, a larger permeation of oxygen near the propane entry may be useful.
- Combination of a conventional fixed-bed reactor with a membrane reactor. In such case, the feed to the fixed-bed reactor contains a small amount of oxygen.

- Use of a catalytic membrane. In this case, part of the membrane is loaded with catalyst, preferentially in the side where propane is feed. The operation principle is the same as when a packed bed of catalyst enclosed in a membrane is employed: the lower oxygen partial pressure in the reaction zone increases the selectivity to the desired product.

Types of Membrane

The membrane employed for this reaction does not need to be selective for oxygen, i.e., a mesoporous membrane may be employed. In such case, the back permeation of hydrocarbon to the shell side must be avoided. This usually requires a significant pressure drop of oxygen. Examples of membranes employed include microfiltration ceramic membranes with the pores filled with silica, nanofiltration ceramic membranes with enamel trips to reduce the permeation, or zeolite membranes.

Alternatively dense ceramic membranes, i.e., oxygen selective, can be employed. In such case, in addition to the improvement in butene selectivity provided by the oxygen distribution and the avoidance of back permeation problems, the previous step of oxygen separation from air may be avoided.

Catalysts

Although in principle any catalyst suitable for oxidative dehydrogenation of butane could be tested in a membrane reactor, the most employed are the simplest ones: vanadium oxide supported on alumina or on magnesium oxide.

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n-C₄H₁₀/CH₄ Separation

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Before treatment, natural gas comes with close to saturation higher hydrocarbons such as ethane, propane, butane, or higher hydrocarbons. It is necessary to remove those compounds for the following reasons:

- Prevent condensation troubles in pipelines: as an illustration, the dew point specification in the US interstate pipeline is fixed at -20°C .
- Propane, butane, or higher hydrocarbons can be valued as liquids and are particularly prized as steam cracker feeds to produce short olefins (ethylene, propylene).
- If the natural gas is used locally as fuel for combustion engines operating compressors or power-generating turbines, the presence of higher hydrocarbons can cause combustion problems or even accelerate aging of the engines.

The conventional technologies used in the industry to remove such “heavies” are condensation or lean oil absorption.

Several companies have been proposing vapor permeation modules to operate heavy hydrocarbon recovery from small natural gas flowstream since the 1990s: *MTR Inc.*, *Borsig*, and *GKSS*. All the membranes in operation are based on silicone-selective layer which offer mixed-gas propane/methane separation selectivity comprised between 3 and 5 (Baker and Lokhandwala 2008; Alpers et al. 1999) and butane/methane separation selectivity ranging from 5 to 10 (Baker and Lokhandwala 2008; Alpers et al. 1999).

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NELF Model

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The nonequilibrium lattice fluid (NELF) model (Doghieri and Sarti 1996; Sarti and Doghieri 1998) allows to calculate the thermodynamic properties of a solute in a glassy polymeric phase. It represents the suitable extension to the nonequilibrium glassy phase of the equilibrium lattice fluid equation of state by Sanchez and Lacombe (1976, 1978) and Lacombe and Sanchez (1976), according to the general rules of the nonequilibrium thermodynamics for glassy polymers (NET-GP) (Doghieri et al. 2004a, 2006; Giacinti Baschetti et al. 2005a), which requires in general that the state of a isotropic homogeneous glassy phase is given by temperature T , pressure p , densities of all solutes ρ_i , and density

NELF Model, Table 1 List of symbols and properties used in the NELF model

	Symbol	Name	Definition/property
Pure component i	ρ_i^*	Characteristic density of pure component i	
	p_i^*	Characteristic pressure of pure component i	
	T_i^*	Characteristic temperature of pure component i	
	r_i^0	Number of lattice sites occupied by a mole of pure component i	$r_i^0 = \frac{M_i}{\rho_i^* v_i^*}$
	v_i^*	Volume occupied by a mole of lattice sites of pure substance	$v_i^* = \frac{RT_i^*}{p_i^*}$
Mixtures	N	Total number of moles	
	T	Temperature	
	p	Pressure	
	ρ	Density	
	ρ_i	Density of species i	$\rho_i = \omega_i \rho$
	ρ_{pol}	Density of polymer species	$\rho_{pol} = \omega_{pol} \rho$
	ω_i	Mass fraction, $i = 1, 2, \dots, N_p$	$\omega_i = \frac{\rho_i}{\rho}$
	ϕ_i	Volume fraction	$\phi_i = \frac{\omega_i / \rho_i^*}{\sum_i \omega_i / \rho_i^*}$
	ρ^*	Characteristic density of the mixture	$\frac{1}{\rho^*} = \sum_i \frac{\omega_i}{\rho_i^*}$
	p^*	Characteristic pressure of the mixture	$p^* = \sum_i \phi_i p_i^* - \frac{1}{2} \sum_i \phi_i \sum_{j \neq i} \phi_j \cdot \Delta p_{ij}^*$
	Δp_{ij}^*	Binary parameter	$\Delta p_{ij}^* = p_i^* + p_j^* - 2(1 - k_{ij}) \sqrt{p_i^* \cdot p_j^*}$
	k_{ij}, Ψ_{ij}	Dimensionless binary parameter	$\Psi_{ij} = 1 - k_{ij}$
	r	Molar average number of lattice sites occupied by a molecule in the mixture	$r = \sum_i x_i r_i$
	T^*	Characteristic temperature of the mixture	$T^* = \frac{v^*}{r} \sum_i x_i r_i^0 \frac{T_i^*}{p_i^*} = \frac{v^* v^*}{R}$
	ε^*	Characteristic energy	$\varepsilon^* = \frac{T^*}{k}$
	v^*	Average close-packed mer molar volume in the mixture	$v^* = \frac{RT^*}{p^*}$
	$\tilde{\rho}$	Dimensionless density	$\tilde{\rho} = \frac{\rho}{\rho^*}$
	$\tilde{T}$	Dimensionless temperature	$\tilde{T} = \frac{T}{T^*}$
	$\tilde{p}$	Dimensionless pressure	$\tilde{p} = \frac{p}{p^*}$
	A^{Eq}	Total equilibrium Helmholtz free energy	$\frac{A^{Eq}}{rNR T^*} = -\tilde{\rho} + \tilde{T} \left[\left(\frac{1}{\tilde{\rho}} - 1 \right) \ln(1 - \tilde{\rho}) + \frac{1}{\tilde{r}} \ln(\tilde{\rho}) + \sum_{i=1}^{N_p+1} \frac{\phi_i}{r_i} \ln(\phi_i) \right]$
	μ_i^{NE}	Chemical potential of solute i in the nonequilibrium glass	$\frac{\mu_i^{(S)}}{RT} = \ln(\tilde{\rho} \phi_i) - \left(r_i^0 + \frac{r_i - r_i^0}{\tilde{\rho}} \right) \cdot \ln(1 - \tilde{\rho}) - r_i - \tilde{\rho} \frac{r_i^0 v_i^*}{RT} \left[p_i^* + \sum_{j=1}^{N_p} \phi_j (p_j^* - \Delta p_{ij}^*) \right] + 1$

NELF Model, Table 2 NELF model pure component parameters for different polymers

Symbol/ acronym	Name	T* [K]	p* [MPa]	ρ^* [g/cm ³]	Source
PC	Poly(carbonate)	755	534	1.275	(Doghieri and Sarti 1996)
TMPC	Tetramethyl poly(carbonate)	761.6	446.4	1.174	(Doghieri and Sarti 1998)
PMMA	Poly(methyl methacrylate)	695	560	1.27	(Doghieri and Sarti 1998)
PEMA	Poly(ethyl methacrylate)	602	567.5	1.221	(Giacinti Baschetti et al. 2005a)
PPO	Poly(2,6-dimethyl-1,4-phenylene oxide)	739	479	1.177	(Doghieri and Sarti 1998)
PSF	Poly(sulfone)	830	600	1.31	(Doghieri and Sarti 1998)
PVAC	Poly(vinyl acetate)	592	510	1.284	(Doghieri and Sarti 1998)
PVC	Poly(vinyl chloride)	736	415	1.458	(Doghieri and Sarti 1998)
HFPC	Hexafluoro poly(carbonate)	716.5	446	1.618	(Sarti and Doghieri 1998)
AF1600	Tetrafluoroethylene (TFE) – 2,2-bis(trifluoromethyl)–4,5-difluoro-1,3-dioxole (BDD) (25–65 mol)	575	280	2.16	(De Angelis et al. 2002)
AF2400	Tetrafluoroethylene (TFE) – 2,2-bis(trifluoromethyl)–4,5-difluoro-1,3-dioxole (BDD) (13–87 mol)	624	250	2.13	(De Angelis et al. 2002)
PTFE	Poly(tetrafluoroethylene)	618	371	2.25	(De Angelis et al. 2002)
PS	Poly(styrene)	750	360	1.099	(Sarti and Doghieri 1998)
PEUT	Poly(ether urethane)	550	450	1.132	(Giacinti Baschetti et al. 2003)
PTMSP	Poly(trimethylsilyl propyne)	610	380	1.125	(Giacinti Baschetti et al. 2005b)
TMSP/ TMSE 70/30	1-trimethylsilyl-1-propyne/1-trimethylsilyl-1-n-hexyne 70/30 copolymer	515	580	1.25	(Giacinti Baschetti et al. 2005b)
TFE/ PMVE49	Tetrafluoroethylene – perfluoromethyl vinyl ether (50.7–49.3 mol)	509	395	2.244	(Prabhakar et al. 2005)
PTMSN	Addition type poly(trimethylsilyl norbornene)	406	360	1.345	(Galizia et al. 2012)
LDPE	Low density poly(ethylene)	693	400	0.883	(Giacinti Baschetti et al. 2005a)

of the polymer species ρ_{pol} (polymer mass per unit volume of the mixture). The latter quantity is the value prevailing in the nonequilibrium state of the glass, at the temperature, pressure, and composition considered; it depends on the thermomechanical prehistory of the polymer phase and is due to the kinetic hindrance offered by the glassy phase which does not allow the polymer density to reach the value minimizing Gibbs free energy at the given T and p. Polymer density must be assigned as additional nonequilibrium state variable, e.g., on the bases of direct experimental or other equivalent information; it represents the departure from

the equilibrium of the glassy phase and is formally treated as an internal state variable (Sarti and Doghieri 1998). From the general results of NET-GP (Doghieri et al. 2004a, 2006; Giacinti Baschetti et al. 2005a), the Helmholtz free energy of the glassy phase is formally given by the same expression of the equilibrium Helmholtz free energy, as a function of T, ρ_i , and ρ_{pol} , where the latter is a nonequilibrium value.

The most relevant result of the model is embodied by the following explicit expression of the chemical potential of each solute *i* in the glassy mixture, as a function of temperature, composition, and polymer density:

NELF Model, Table 3 NELF model pure component parameters for different solutes

Symbol/acronym	Name	T* [K]	p* [MPa]	ρ^* [g/cm ³]	Source
H ₂	Hydrogen	46	37	0.078	(Doghieri and Sarti 1998)
O ₂	Oxygen	180	214	1.25	(De Angelis et al. 1999)
N ₂	Nitrogen	145	160	0.943	(Doghieri and Sarti 1998)
He	Helium	9.3	4	0.148	(De Angelis et al. 2007)
Ar	Argon	190	180	1.31	(De Angelis et al. 2006)
Xe	Xenon	304	351	3.36	(De Angelis et al. 2007)
CH ₄	Methane	215	250	0.5	(Doghieri and Sarti 1998)
CO ₂	Carbon dioxide	300	630	1.515	(Doghieri and Sarti 1998)
SO ₂	Sulfur dioxide	430	630	1.734	(De Angelis et al. 2006)
N ₂ O	Nitrous oxide	319	524	1.408	(De Angelis et al. 2007)
H ₂ O	Water	670	2,400	1.05	(De Angelis et al. 2007)
CH ₃ OH	Methanol	510	1,080	0.9	(De Angelis et al. 2007)
C ₂ H ₅ OH	Ethanol	470	880	0.915	(De Angelis et al. 2007)
C ₃ H ₇ OH	1-propanol	500	700	0.913	(Galizia et al. 2012)
(CH ₃) ₂ CO	Acetone	484	533	0.92	(De Angelis et al. 2007)
CH ₃ CN	Acetonitrile	505	910	0.855	(Giacinti Baschetti et al. 2003)
VCM	Vinyl chloride	450	390	1.115	(Doghieri and Sarti 1998)
CF ₄	Tetrafluoromethane	230	265	1.92	(De Angelis et al. 1999)
C ₂ F ₆	Perfluoroethane	296	227	1.95	(De Angelis et al. 1999)
C ₃ F ₈	Perfluoropropane	335	225	2.05	(De Angelis et al. 1999)
C ₆ H ₆	Benzene	523	444	0.994	(De Angelis et al. 2007)
C ₇ H ₈	Toluene	543	402	0.966	(Giacinti Baschetti et al. 2005a)
C ₂ H ₄	Ethylene	295	365	0.68	(Doghieri and Sarti 1998)
C ₂ H ₆	Ethane	320	330	0.64	(De Angelis et al. 1999)
C ₃ H ₈	Propane	375	320	0.69	(De Angelis et al. 1999)
n-C ₄ H ₁₀	n-Butane	430	290	0.72	(De Angelis et al. 2002)
n-C ₅ H ₁₂	n-Pentane	451	304	0.752	(Prabhakar et al. 2005)
n-C ₆ H ₁₄	n-Hexane	476	298	0.77	(Prabhakar et al. 2005)
c-C ₅ H ₁₂	c-Pentane	478	389	0.88	(Prabhakar et al. 2005)
c-C ₆ H ₁₄	c-Hexane	497	383	0.902	(Prabhakar et al. 2005)
n-C ₇ H ₁₆	n-Heptane	498	295	0.780	(Galizia et al. 2012)
n-C ₈ H ₁₈	n-Octane	502	308	0.815	(Sanchez and Lacombe 1976)
n-C ₉ H ₂₀	n-Nonane	517	307	0.828	(Sanchez and Lacombe 1976)
n-C ₁₀ H ₂₂	n-Decane	530	304	0.837	(Sanchez and Lacombe 1976)
n-C ₁₁ H ₂₄	n-Undecane	542	303	0.846	(Sanchez and Lacombe 1976)
n-C ₁₂ H ₂₆	n-Dodecane	552	301	0.854	(Sanchez and Lacombe 1976)

$$\begin{aligned}
 \frac{\mu_i^{(S)}}{RT} = & \ln(\tilde{\rho}\phi_i) - \left(r_i^0 + \frac{r_i - r_i^0}{\tilde{\rho}} \right) \\
 & \cdot \ln(1 - \tilde{\rho}) - r_i \\
 & - \tilde{\rho} \frac{r_i^0 v_i^*}{RT} \left[p_i^* + \sum_{j=1}^{N_p} \phi_j (p_j^* - \Delta p_{ij}^*) \right] + 1
 \end{aligned}
 \tag{1}$$

The quantities used by the model are defined in Table 1. The model expressions contain pure component parameters and one binary interaction parameter for each couple of components in the mixture. The pure component parameters for the polymers are obtained from volumetric data above the glass transition temperature (Doghieri

and Sarti 1996; Sarti and Doghieri 1998); alternative techniques have been proposed for the polymers degrading before glass transition is reached (Galizia et al. 2012). The pure component parameters for gases are obtained from volumetric data; for vapors and liquids, vapor pressure data are also used.

A collection of pure component parameters for polymers of interest in membrane separations is reported in Table 2, while for relevant penetrants, pure component parameters are reported in Table 3. The binary interaction parameters are generally used as fitting quantities, even though a predictive method has been proposed (Rodgers and Sanchez 1993), and often the first order approximation of $k_{ij} = 0$ is also acceptable. Remarkably, the nonequilibrium model, using T and ρ_{pol} as input, is much less sensitive to the binary parameter than the corresponding equilibrium model, using temperature and pressure as input.

The phase equilibrium (or more properly pseudo-equilibrium) conditions between the glassy nonequilibrium phase and an external fluid phase, either gaseous or liquid, are represented as usual:

$$\mu_i^{(S)} = \mu_i^{(\text{external fluid})} \quad (2)$$

By using Eq. 1 for the chemical potential of species i dissolved in the glassy phase and usual equilibrium expression for the chemical potential of species i in the external fluid phase, from Eq. 2 one obtains solubility isotherms for pure penetrants (Doghieri and Sarti 1996, 1998; Sarti and Doghieri 1998; Giacinti Baschetti et al. 2001; De Angelis et al. 2007) as well as for mixed gases (Doghieri et al. 2004b; Minelli et al. 2011), in pure glassy polymers, in polymer blends (Grassia et al. 2004), as well as in glassy-mixed matrices (Maria Grazia De and Sarti 2008; Maria-Chiara et al. 2010). The model is also suitable to calculate the solubility of liquids in glassy polymers (Sarti and De Angelis 2012).

Whenever the binary interaction parameters are known from data above the glass transition

temperature, and polymer density is known, the model is entirely predictive (Doghieri and Sarti 1996; Sarti and Doghieri 1998). Under non-swelling conditions the polymer density remains equal to the value of the pure unpenetrated polymer (Doghieri and Sarti 1998; Giacinti Baschetti et al. 2001). At high pressures and for swelling penetrants, volume dilation of the polymers is required, e.g., through the use of a swelling coefficient (Giacinti Baschetti et al. 2001). Remarkably, the model also shows that in all cases, both at low and high free volume, it is sufficient to consider only molecules dissolved in the glassy phase, without the need of an arbitrary differentiation between hypothetically different populations of penetrant molecules.

The interested users can freely download the code for the solubility isotherms of binary mixtures (<http://serwebdicma.ing.unibo.it/polymers/index.htm>).

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Neuronal Regeneration

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Synonyms

Neuronal tissue regeneration

The expression “neuronal regeneration” refers to all the strategies available for the regrowth, repair, or the substitution of neuronal cells or cell products after an injury causing damages and/or degeneration of the nervous system (NS). In higher organisms like animals and human beings, the regenerative ability of the nervous system is very limited. The NS consists of two connected sections called central and peripheral systems. The central nervous system (CNS), in charge of the behavior control and the information processing, includes the brain and the spinal cord, whereas the peripheral nervous system (PNS) is made up of cranial, spinal, and autonomic nerves, able to coordinate locomotion, sensory perception, and homeostasis. Intended for the transmission and the report of signals and information between the body and the brain, the

neurons are the main units for both the systems, but due to the different glial cell composition, a discrepancy between the regenerative capabilities in the central nervous system and the peripheral nervous system is recorded. Glia is constituted of nonneuronal cells serving to provide physical and chemical support and protection to neurons. Schwann cells and oligodendrocytes are respectively the main glia components of the PNS and the CNS. They are responsible of the axons myelination allowing rapid and efficient signal transmission and impulse conduction between the two systems, whereas the central astrocytes serve the maintenance of the homeostasis and the recycle of the neurotransmitters. When an injury occurs and the peripheral axons are severed, leading to the Wallerian degeneration, macrophages and monocytes migrate in the injured site to remove myelin and axon debris. Schwann cells proliferate in order to substitute glial cells lost during injury and initiate the production and secretion of laminin and fibronectin, which provide the path for the regeneration. Moreover, they upregulate the expression of adhesion proteins (NCAMs), cadherins (N-cadherin), and other neurotrophic factors (BDNF, CNTF, GDNF) involved in the axonal regeneration across the area of injury and lead the formation of growth cones in the proximal damaged axons. Unlike peripheral glia, oligodendrocytes in the CNS are not able to proliferate, and then cells lost to injury are not replaceable. Furthermore, the growth-promoting activity of the central glia is not enough to ensure the conductive environment for the axonal regrowth due to the over expression of inhibitor factors of the axon growth. After a trauma or an injury, the production of neuroprotective factors is quite limited and eventually not enough to oppose the two main mechanisms occurring in the central nervous system. First, the apoptotic phenomena affecting the surrounding of the damaged area over a great distance, due to the secretion of members of the transforming growth factor family (TGF) that largely promote cell death. Secondly, the proliferation of glial cells in quiescent state and the consequent formation of a glial scar acting as physical barrier for the axonal regeneration. Astrocytes actually produce and secrete specific

factors, such as NOGO proteins, NI-35, chondroitin sulfate proteoglycans, and keratan sulfate proteoglycans, known to be inhibitors of the remyelination and axon repair (Steward et al. 2013; Allodi et al. 2012). Then, the modulation of the regenerative process in the nervous system lies on different approaches depending on the site and the extension of the injured area. Independently on the causes, an injury affects the nervous system with the inability of neuronal cells to transmit impulses to specific regions of the nervous system. In order to restore the functionalization, one of the three specific repair mechanisms must occur: the regrowth of the neuronal damaged axons, the recovery of the axonal function, or the substitution of the neurons that have been lost through the generation of new neuronal cells. Each one of these regenerative methods stands as alternative to the gold standard treatments, represented by the coaptation and the nerve graft implantation. The first one consists in the surgical reparation of small nerve gap (<8 mm) resulting after an injury, and the second one consists in the implantation of grafts regardless the size of the gaps. Generally autografts, which have no risk of immune reactions, are the first choice in the nerve injury treatment, but allografts and xenografts are also available. Therefore, none of them allow to reach a full functional recovery and many drawbacks are possible.

Cell Replacement or Cell Therapy. When a wide area of the nervous system has been damaged by a trauma or a degenerative pathology, a replacement of the neuronal cells can be obtained using stem cells. Neural stem cells (NSC) are available from the hippocampus, spinal cord, fetal brain, and neural retina and due to the ability to self-renew can differentiate in neurons, astrocytes, and oligodendrocytes in order to substitute cells lost in the injury. Amyotrophic lateral sclerosis (ALS), spinal muscular atrophy (SMA), main motor neuron disorders, and Parkinson's disease (PD) are the focus of the neural stem cell strategies. NSC not only can be integrated into host nervous system but also have been engineered to act as delivery vehicle for neuroprotective growth factors like the GDNF

and IGF-1, resulting in an increase of the spinal motor and the dopaminergic neuron survival (Tysseling and Kessler 2011). Pluripotent stem cells have been also successfully used as strategy for the neuronal regeneration. They represent a perfect in vitro system for developmental studies and can be not only differentiated in neurons but reprogrammed to form stem cells facilitating the replacement of degenerated neurons from autologous sources avoiding grafts rejection in the patients (Steward et al. 2013).

Drug Delivery. Many natural and synthetic molecules have shown to possess neuroprotective and neurogenerative properties. The administration of neurotrophic factors demonstrated an improvement of the regenerative process in both the central and the peripheral nervous systems. The intact blood-spinal cord barrier represents an obstacle in reaching the brain and the spinal cord, but generally after injuries or degenerative processes, several parts result to be compromised; therefore, neurotrophins and drugs administered can overcome the barrier reaching the site of action. Carrier, microcarrier, microspheres, liposomes, and hydrogels are the devices available for the controlled release, and synthetic or natural polymers, extracellular matrix derived biomaterials, carbon nanoparticles, and ions complexes represent only a few of the biomaterials usable for their preparations (Tysseling and Kessler 2011; Gu et al. 2014). Moreover, not only spinal cord and nerve regeneration have been achieved, but due to this strategy central diseases such as Parkinson's and Alzheimer's are possible. In fact, the controlled release of dopamine and β -amyloid inhibitors represents today the best treatment available for the neurodegenerative pathologies in combination with the cell transplantation. Moreover, in order to avoid multiple drug injections and to increase the delivery time in the selected area, mini-pumps are available and surgically implantable in patients for the treatment of the chronic pain and the degenerative diseases.

Nerve Conduit, Scaffolds, and Channels. The protection of the injured site from inhibitor factors and apoptotic/inflammatory phenomena is of

main importance in order to increase the regenerative process in the nervous system. This is the reason why scaffolds, channels, and conduits have been purposely made to protect the severed areas during the regeneration and tested in in vitro and in vivo studies. With the aim of recreating a permissive environment for the neurite and axonal growth, these synthetic devices consisting of polymers and hydrogels in form of tubes or fibers possess morphological, chemical-physical, and mechanical specific properties. Topography, mechanical strength, biodegradation, porosity, and dimensions are necessary to induce cell adhesion, proliferation and differentiation, to allow the nutrient and growth factor supply, to remove the metabolites and inhibitors, and to avoid the device collapsing during the regenerative process after the implantation (Sedaghati et al. 2014; Morelli et al. 2010). Collagen, laminin, fibronectin, polycaprolactone, polylactic acid, and chitosan tubes are allowed to build high-quality guides for the neural repair. In addition, in the last decade, the nerve conduits have been further developed and leveled up through the combination with supportive cells and the growth factors incorporation. Alternatively, neural stem cells and pluripotent cells are seeded in the lumen of the tubes, and they stimulate the release of diffusible growth factors in order to induce the neurite outgrowth and axonal regeneration in the insulated area. On similar lines of the drug delivery, growth factors and neuroprotective agents are encapsulated in the scaffolds or incorporated in the biomaterials and then let diffuse towards the severed site. This new approach increases the neural regeneration guiding the axonal growth in both the central and peripheral nervous systems.

Despite the autografts still remain the gold standard for the treatment of the nervous system injuries, the promising results recorded in the biomaterials field represent the best alternative in the development of new regenerative approaches, based on the controlled drugs and factors release, the guidance of the axonal regrowth, and the transplantation of cells in the selected area.

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Neuronal Tissue Regeneration

► Neuronal Regeneration

NF Membrane Characterization Methods

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A variety of techniques and approaches are routinely used for characterizing the physical and chemical properties of nanofiltration (NF) membrane surfaces (Web Report #4102 2012). The main fundamental properties which are usually characterized, in no particular order, include molecular weight cut-off (MWCO), pore size (and pore-size distribution), pure water flux, surface charge (or zeta potential), hydrophobicity and/or hydrophilicity, and membrane morphology and surface roughness.

The molecular weight cut-off is found by filtering a range of molecules (very often polyethylene glycol (PEG)) with known molecular weights. The molecular weight of the molecule that is 90 % retained by the membrane is usually defined as the MWCO of that membrane.

The pore size of the membrane may be found via atomic force microscopy (AFM) measurements or more usually by filtering an uncharged molecule like glucose and fitting the Nernst-Planck equation for uncharged solutes to the results, using the membrane pore size as the fitting parameter. NF membranes are typically rated by MWCO rather than nominal pore size.

The flux or pure water flux for a membrane is typically expressed as volume per area per unit of time. Flux is used to express the rate at which pure water permeates a NF membrane. Typical units of measurement are gallons per square foot per day (i.e., GFD or GSFD) or liters per square meter per hour ($\text{l/m}^2/\text{h}$)

Streaming potential measurements are most often used to calculate the zeta potential of an NF membrane surface. This is an indicator of the membrane surface charge under variable solution chemistries.

Measuring the contact angle that is formed when a droplet of water is placed on the membrane surface is used to quantify the hydrophobicity/hydrophilicity of the membrane surface.

AFM and scanning electron microscopy (SEM) are both powerful techniques used to quantify and visualize the morphology or roughness of membrane surfaces. SEM in particular is used to visualize the cross-sectional morphology of NF membranes.

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NF Membranes

► Nanofiltration Membranes

Nichel Recovery by Liquid Membrane

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Heavy metal removal from various industrial wastewaters is a major concern, since they are often present at significant levels. Among the numerous industrial sectors that contribute to environmental pollution with these metals, such as dyeing, mining, electroplating, nuclear power operations, aerospace, and battery manufacturing processes, the metal finishing industry is very important due to the large number of locations as their geographical dispersion. Heavy metals differ from organic substances because they are not biodegradable (Lothongkum et al. 2009). Thus, they can accumulate in living tissues, causing various diseases and disorders, since they are toxic to human beings and organisms even at very low concentrations (Hassaine-Sadi et al. 2012). Among these metals, chromium, nickel, zinc, copper, and cadmium are the most abundant ones.

The main way of water contamination by heavy metals is the discharge of liquids effluent with relatively low but harmful concentration. As a consequence, the appropriate treatment of high-volume wastewater containing low concentrations of heavy metals is very important, and in addition, the discharge regulation is progressively becoming more stringent. The World Health Organization recommends the toxic limits of permissible concentration of Ni in wastewaters at a level of 1 mg/L as insoluble compounds, 0.1 mg/L as soluble compounds, 0.05–0.12 mg/L as nickel carbonyl, and 1 mg/L as nickel sulfide. Many countries have regulations of the maximum

permissible concentration of nickel in industrial wastewaters with values in the order of 1 mg/L.

Chemical precipitation is extensively used to treat nickel-bearing wastewater, resulting in the production of a large amount of toxic chemical sludge which disposal/treatment is a very costly affair, and it is not eco-friendly (Molinari et al. 2009). Other convectional methods, such as filtration after neutralization, ion exchange, and adsorption, are not selective, and thus, no metal recovery is achieved. Besides, they are expensive methods and not efficient enough to reduce nickel concentration below the permissible concentrations.

Transport of metal ions across a liquid membrane (LM) is a powerful technology combining extraction and stripping into a one-step process (Güell et al. 2008; Walkowiak and Kozłowski 2009). LM systems include bulk liquid membrane (BLM), emulsion liquid membrane (ELM), and supported liquid membrane (SLM). The lower capital and operating costs, the low energy and extractant consumed, and the high selectivity are the main advantages of LM systems with respect to the traditional separation techniques. Thanks to these characteristic, LM-based techniques permit to obtain the recovery of heavy metal ions and the production of water with good quality, resulting into both environmental and economic benefits.

The selective separation of nickel from various aqueous media containing nickel and cobalt, that is, an important problem in hydrometallurgy, can be carried out by using ELM (Longquan et al. 1997; Kumbasar and Tutkun 2008). Ni and Co possess aqueous similar chemical behavior, because they are metal of the transition series adjacent in the periodic table, but some differences exist. In ammoniacal environment (Kumbasar 2009) the complex $\text{Co}(\text{NH}_3)^{2+}$ is readily oxidized to $\text{Co}(\text{NH}_3)^{3+}$ with addition of hydrogen peroxide, while the nickel complex $\text{Ni}(\text{NH}_3)^{2+}$ is not oxidized. In these conditions the nickel ammine complex can be selectively extracted using an acidic extractant (e.g., 5,7-dibromo-8-hydroxyquinoline (DBHQ)) by the following reversible pH-dependent reaction:



The concentration of complexing agent (e.g., ammonia) in the feed phase, the pH of the feed and of the strip aqueous phases, the composition of the LM phase (extractant concentration, surfactant concentration, modifier concentration), the mixing speed of feed solution, the presence of complexing agent and its concentration in the strip phase, and the feed/strip volumetric ratio are the most important operating variables influencing the permeation of nickel across a LM and then membrane selectivity.

The selective recovery of nickel ions from wastewater of stainless steel manufacturing plants can be efficiently carried out by hollow fiber supported liquid membranes (HFSLM). The type of extractant and its concentration in the LM phase, the pH of the feed phase, the stripping solution concentration (i.e., pH), the flow rates of feed and stripping solution, and the volumetric ratio of feed to stripping solutions represent the most important parameters affecting system selectivity (Lothongkum et al. 2009). Two or more HFSLM modules can be placed in series, obtaining satisfactory nickel recovery and an aqueous effluent with concentration within the common permissible limits.

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Nickel, Recovery of

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Recovery of nickel from aqueous effluents by membrane operations.

Nickel, combined with other elements, occurs naturally in the earth's crust, and the earth's core is composed of 6 % nickel. It is found in all soil and is also emitted from volcanoes. Pure nickel is a hard, silvery-white metal. It has properties which make it a favored alloy. The nickel alloys are used in making metal coins, jewelry, and industry. Most nickel is used to make stainless steel. It is added to metals to increase their hardness, strength, and corrosion resistance. Nickel forms compounds with many elements including chlorine, sulfur, and oxygen. Most of these nickel compounds are fairly water soluble. Nickel and its compounds have no characteristic odor or taste. Nickel compounds are used for nickel plating, to color ceramics, to make some batteries, and as catalysts that increase the rate of chemical reactions. Nickel is released into the atmosphere during nickel mining and by industries that make or use nickel, nickel alloys, or nickel compounds. These industries also might discharge nickel in wastewater. Nickel is also released into the atmosphere by oil-burning

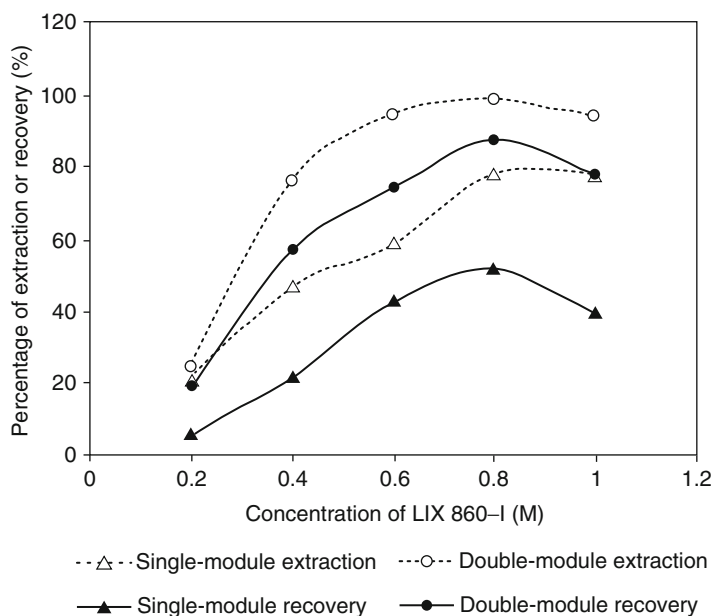
Nickel, Recovery of, Table 1 Removal of Ni^{2+} from wastewater using membrane filtration (Reproduced with permission from Elsevier)

Technique	Initial Ni^{2+} concentration (mg/L)	Removal efficiency (%)	Operating pressure	Working pH
Micellar-enhanced UF	29.35	46–54	0.5–2	5.5
	10	88–99.2	1–5	5–3–6.3
	0.95–1.76	73.6–85.1	3	3.5–5
Complexation – UF	50	98–99	2–4	3–9
	58.71	31.5–98.2	5	7–9
Chelation – UF	25	24.1–94.2	2–5	NA
Flotation – UF	3.3	98.5	<1	8–10
RO	3.36	96.8	20	3.6–7
	44–169	99.7	11	6.5–7.5
	500	99.5	5	4–11
NF	29.35–880.75	89–96	2.8	3–7
	5.87	92–93	2–8	4–8
	5–250	92–98	4–20	2–8
	5–10	96.87–97.96	4–20	2–10

UF ultrafiltration, RO reverse osmosis, NF nanofiltration, NA not available

Nickel, Recovery of,

Fig. 1 Percentages of extraction and recovery of nickel ions from a single-module and double-module operations at different concentration of LIX 860-I: pH of feed solution = 4, stripping solution $[\text{H}_2\text{SO}_4] = 1.5 \text{ M}$ (single module) and 2.0 M (double modules), $Q_{\text{feed}} = Q_{\text{strip}} = 100 \text{ mL/min}$, and $V_{\text{feed}}:V_{\text{strip}} = 3500:3500 \text{ mL}$ (Reproduced with permission from Elsevier)



power plants, coal-burning power plants, and trash incinerators (Toxicological Profile for Nickel 2013).

Nickel is removed from electroplating wastes by treatment with hydroxide, lime, and/or sulfide to precipitate the metal (HSDB 2004). Nickel is removed/recovered from various wastes, such as spent solutions, spent batteries, spent Ni–Cd

batteries, spent Ni–MH batteries, spent catalysts, waste electrical and electronic equipment by chemical precipitation, ion flotation, ion exchange, membrane filtration, adsorption, crystallization, solvent extraction, electrodialysis, electrowinning, and pyrometallurgical and hydrometallurgical techniques (Coman et al. 2013). The removal efficiency of nickel by some membrane

separation methods is shown in Table 1 (Coman et al. 2013). Eisenmann (1981) observed that the electrodialysis (ED) can concentrate the nickel 50- to 100-fold than that of reverse osmosis, and ED is better than the ion exchange system. Castelblanque and Salimbeni (2004) reported recovery of nickel from cleaning baths in the electrodeposition of nickel by NF and RO with encouraging results. The recovery of nickel from stainless steel cold-rolled plate process by hollow fiber-supported liquid membrane (HFSLM) with the help of extractants di(2-ethylhexyl) phosphoric acid (D2EHPA), bis(2,4,4 trimethylpentyl) phosphinic acid (Cyanex 272), bis(2,4,4 trimethylpentyl) dithiophosphinic acid (Cyanex 301), and 5-dodecylsalicylaldoxime (LIX 860-I) gave fruitful results (Lothongkum et al. 2009). Lothongkum et al. (2009) found that the nickel recovery with a single-module operation was 58 %, whereas by double-module operation recovery reached 87 % using the LIX 860-I extractant (Fig. 1). Researchers showed (de Voorde et al. 2004; Darvishi et al. 2005) that the synergistic effect of the combination of the extractants was more than that when the extractants are used separately. The extractant di-2,4,4-trimethylpentyl mono-thio-phosphinic acid (Cyanex 302) was found to be more suitable than the other in the recovery of nickel (Darvishi et al. 2005; Dimitrov et al. 2008).

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Niobium (Nb), Vanadium (V), and Tantalum (Ta) Alloys, Membranes of

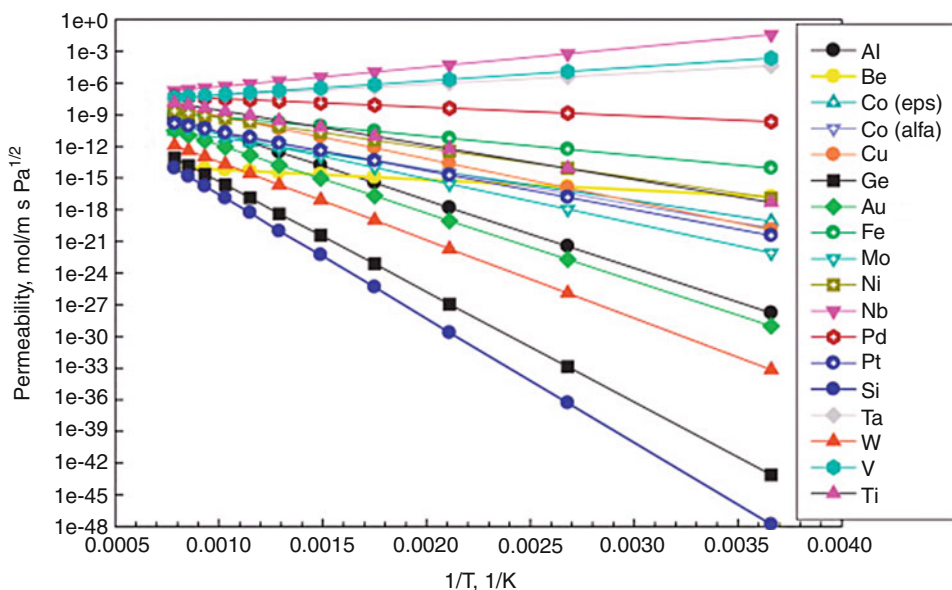
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Niobium (Nb), vanadium (V), and tantalum (Ta) are the so-called refractory metals, and they have much higher hydrogen permeability at temperatures below 300 °C in comparison to palladium as shown in Fig. 1. These metals are much cheaper and have greater tolerances to high temperatures compared to palladium (Gallucci et al. 2013). Therefore, studies on replacement of Pd by these metals and their alloys have increased during the last years (Mundschau et al. 2006).

General Aspects

These membrane materials have two main drawbacks: they are easy to oxidize and are not able to dissociate and recombine hydrogen molecules. The most used catalytic materials to be coated on the surface of the refractory materials in order to enable hydrogen transport are Pd, Pt, Ni, Rh, Ir, Co, and alloys thereof (Dye and Snow 2001). The



Niobium (Nb), Vanadium (V), and Tantalum (Ta) Alloys, Membranes of, Fig. 1 Hydrogen permeability through several metals as a function of temperature (Basile et al. 2008)

thicknesses of these catalytic layers are usually in the order of hundreds of nm, and thus the cost of using a noble metal instead of Pd does not contribute significantly to whole cost of the membrane. Pure niobium, vanadium, tantalum, and also Zirconium have very high permeabilities, but they are also very brittle. On the contrary, several alloys of these metals are also non-embrittling, making them good candidates for hydrogen purification membranes (Yang et al. 2006; Dolan 2010; Dolan et al. 2011; Ishikawa et al. 2011; Paglieri et al. 2011; Wolden et al. 2013).

Niobium, Vanadium, and Tantalum Alloys

According to Yukawa et al., V-based alloys expect to possess stronger resistance to hydrogen embrittlement than Nb-based alloys (Yukawa et al. 2011). When the composite membranes work at elevated temperature ($>400^\circ\text{C}$), the diffusion between the core component and the catalytic layer may occur, causing oxidation of the core metal and a resulting hydrogen permeability

reduction (Behr et al. 1988). Behr et al. recommend the use of Pd-Cu, Pd-Ag, and Pd-Y catalytic layer with Nb, Ta, Ti, and V core metals saturated with Cu, Ag, or Y in order to reduce the driving force for interdiffusion (Behr et al. 1985). Another approach is to use interdiffusion barrier layers, such as oxides, sulfides, and selenides (Dye and Snow 2001; Edlund and McCarthy 1995). And another approach is to use an alloy component that has catalytic activity. Hara et al. proposed ZrNi alloy where Ni acts as the catalytic part and Pd-based layer is not needed (Hara et al. 2002). Another important problem working at high temperatures is that the thin catalytic layer may be delaminated from core membrane due to the difference in thermal expansion coefficient of each part. Mundschau et al. defined the mismatch of thermal expansion coefficient of Pd in comparison to V, Ta, Nb, and Zr at different temperatures, and Pd-V composite membrane has the best match of thermal expansion coefficient (Mundschau et al. 2006). Many amorphous alloys crystallize at high temperatures (over the crystallization temperature (T_x) or glass transition temperature (T_g) of the alloys) and lose the properties that they have as amorphous structures (Dolan

et al. 2006). This is the case of Zr-based alloys that have a T_g around 550–600 °C and are not suitable for high-temperature hydrogen separation. Finally, the resistance to poisoning (e.g., with sulfur) depends mainly on the nature of the deposited catalytic layer, so if the whole membrane has to resist a specific sulfur content, a suitable Pd alloy layer should be chosen (Mundschau et al. 2006).

Membrane Preparation

The most common techniques for the preparation of the refractory metal (Nb, V, Ta, Zr) alloy membrane preparation are rolling and melt spinning (Dolan 2010). Films of above 30 μm -thick films are prepared using these techniques. Then, Pd-based alloy thin catalytic layers are needed on both surfaces of the refractory metal, and other thin film deposition techniques are used such as physical vapor deposition. The future membranes should be composed of thinner refractory membranes and should be supported on porous supports as in the case of palladium-based membranes.

Membrane Commercialization

REB Research and Consulting produces and offers refractory metal-based tubular membranes: tantalum- and niobium-based membranes coated with Pd.

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NIPS

► [Nonsolvent Induced Phase Separation Process \(NIPS\) for Membrane Preparation](#)

NOM-Based Membrane Fouling

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Definition

NOM or natural organic matter is the complex mixture of organic material that can be found in surface or groundwater and can contribute to one form of membrane fouling by accumulating on the surface and/or in the membrane pores resulting in reduced permeate flux or fouling.

Overview

Various fractions in natural organic matter (NOM) and particulate/colloid matter (C/P) are known to significantly contribute to fouling of ultrafiltration (UF) membranes. NOM originates through contact of the water with dead and living organic matter. These components may contribute in different ways to fouling and may require different approaches for membrane regeneration. Fouling may be reversible or irreversible, and this will depend not only on the chemical and physical properties of the membrane (e.g., molecular weight cutoff (MWCO)), but also the configuration of the membrane system (e.g., flat sheet vs. hollow fiber) and other factors such as the nature of the upstream treatment, membrane flux, flow regime, and filtration time. Interaction of the NOM components may also have an influence on the fouling, and this may depend on whether the interaction occurs in the water matrix or at the level of the membrane as the fouling occurs or both. Interactions are not restricted to NOM components but can also occur between other components in the water matrix, such as divalent cations. Broad classification of the NOM constituents would identify the biopolymer fraction, which includes proteins, polysaccharides, and humic substances. Another concern related to NOM, as it pertains to drinking water,

is that reactions between NOM and the commonly used disinfection agent chlorine can result in the formation of disinfection by-products which have been identified as possible carcinogens.

Cross-References

- ▶ [Fouling In Membranes](#)
- ▶ [Irreversible Fouling](#)
- ▶ [Membrane Fouling](#)

Nominal Molecular Weight Cutoff (NMWCO)

- ▶ [Molecular Weight Cutoff](#)

Noncellulosic Membranes

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Noncellulosic membrane is a membrane system without any cellulosic units. Typical noncellulosic membranes include inorganic membranes, synthetic polymer membranes, and natural polymer (excluded cellulosic materials) membranes. One type of inorganic membrane, which contains zeolite, has been used in reverse osmosis, ultrafiltration, and pervaporation (Ulbricht 2006). Synthetic polymer membranes include membrane systems applied over a broad range of the filtration spectrum from microfiltration to reverse osmosis. Representative synthetic polymer membranes for microfiltration and ultrafiltration membranes include polyacrylonitrile (PAN), polysulfone (PSU), polyethersulfone (PES), and polyvinylidene fluoride (PVDF) (Ma et al. 2012). The barrier layer in synthetic polymer membranes for nanofiltration and reverse

osmosis applications typically consists of highly cross-linked polyamide made by interfacial polymerization (Petersen 1993). Natural polymer membranes include protein membranes and noncellulosic polysaccharide membranes, consisting of different sugar units. Selective examples include silk membranes fabricated by electrospinning and chitin (chitosan) composite membranes (Ma et al. 2011a; Yoon et al. 2006; Ki et al. 2007).

The development of cellulosic membranes occurred relatively earlier than that of non-cellulosic membranes (Edgar et al. 2001). Noncellulosic membranes have achieved higher filtration efficiency and durability when compared with those of cellulosic membranes. For example, noncellulose membranes exhibit high chemical resistance and pH tolerance by avoiding the disadvantages of cellulosic membranes composed of glucose units linked with ether bonds (Chenoweth 1986). However, low cost has always been the merit of cellulose and cellulose derivative membranes.

With the introduction of nanotechnology, nanocomposite membranes have overcome many of the obstacles in membrane quality, including higher flux and lower fouling rate. Natural and synthetic, inorganic and organic, and cellulosic and noncellulosic materials can be integrated together to enhance the membrane performance and retain cost-effectiveness. Therefore, nanocomposite membranes are likely the direction in future filtration applications (Ma et al. 2011b).

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Noncovalent Binding for Polymer Surface Modification

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The polymer surface modification by non-covalent binding is obtained by electromagnetic interactions between molecules that can be generally classified into ionic interactions, hydrogen bond, and van der Waals forces. The surface modification through van der Waals attraction and/or hydrogen bonding is a simple method to improve membrane surface properties. The surface modification by non-covalent binding is obtained by coating. Coating a membrane surface with a thin layer of polymers or surfactants permits to optimize hydrophilicity, smoothness, and surface charge of the membrane surface. Thus, the surface-modified membranes have better performance and antifouling characteristics than the base membranes. Many hydrophilic polymers, such as PVA, PAA, PEG-based hydrogels, and chitosan have been coated on different MF, UF, NF, and RO membranes using casting, adsorption, or filtration techniques. The first studies in the field of the membrane coating concerned the modification of UF membranes to reduce their fouling with proteins (Nystrom 1989).

In the casting technique, a polymer is casted on the membrane and then the coated membrane is immersed in the coagulation bath to have the precipitation of the polymer. Asatekin (Asatekin et al. 2009) prepared novel composite NF membranes by casting of the synthesized amphiphilic copolymer PAN-graft-poly(ethylene oxide) (PAN-g-PEO) on UF PAN membranes.

In the case of the adsorption techniques, the membrane surface is modified putting in contact the membrane with a solution of different polymer, and then after solvent evaporation, a thin film of a different polymer forms a new surface. The adsorption can occur on the surface and inside the pores on the pore walls. Maartens (Maartens et al. 2002) used the adsorption of the nonionic surfactants Triton[®] X-100 and Pluronic[®] F108 for the surface modification of tubular UF PES membranes, which were used for filtering the pulp and paper effluents. Triton[®] X-100 is adsorbed to the membrane by hydrophobic interaction with hydrophobic C₆H₄ group. Ba et al. (2010) used the adsorption of water-soluble polymers such as PVA, poly-acrylic acid (PAA), and polyvinyl sulfate-potassium salt (PVS) on the surface of the positively charged P84-PEI membrane to form a protective coating layer to improve membrane fouling resistance.

In the filtration technique, the surface modification is obtained by filtration of a solution containing the polymer. PVA-coated thin film composite (TFC) membranes were obtained by filtration of aqueous solutions containing PVA and cross-linking agents through the porous membrane support, followed by heat treatment (Liu et al. 2000). A PVA gel layer was formed on the surface and in the pores of the modified membranes. The modified membranes showed higher antifouling properties with respect to the unmodified membranes during UF of the pepsin solutions. The UF PES membranes containing negatively charged sulfonic acid group on the surface were obtained by filtration of an aqueous solution of poly(sodium 4-styrenesulfonate) (PSS) for about 100 min using a dead-end filtration cell (Reddy et al. 2003).

A new coating method based on supramolecular assembly very suitable for membrane surface modification is layer-by-layer (LBL) technique

(Decher 1997) in which the assembly is obtained by means of alternative adsorption of linear polycations and polyanions. This technique not only creates a charged skin layer but also allows for a better control of the thickness, charge density, and hydrophilicity of the active skin layer. The only condition for the use of the self-assembly method is that the base membrane must be able to adsorb the first polyelectrolyte layer by means of ionic bonds.

The membrane modified by non-covalent binding is employed in ultrafiltration process as antifouling membrane (Luo et al. 2005) in gas separation process to improve membrane separation performances (Widjojo et al. 2007), in the vapor separation of a wide variety of volatile compounds (Zhen et al. 2006). Indeed, the PVDF hollow-fiber membrane coated with PDMS exhibited very high removal efficiency (>90 %) for all the following VOCs, benzene, chloroform, acetone, ethyl acetate, and toluene. However, despite the flexibility surfaces modification by non-covalent binding interactions to change the hydrophilicity, smoothness, and charge of the membrane surface, their main drawback is a limited stability of the modified layer with time, because of possible desorption of the coated/adsorbed polymers than the modification process can be repeated.

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Noncrystalline

- [Amorphous Fluoropolymers](#)
- [Amorphous Perfluoropolymers](#)

Nondispersive Gas–Liquid Contactor

- [Gas–Liquid Membrane Contactor](#)
- [NELF Model](#)

Nonfluorinated Membranes: Fuel Cell Applications

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Non-fluorinated membranes for fuel cell applications are a class of ionomeric membranes in which the ionogenic groups, responsible for the proton conduction properties, are attached to a fluorine-free polymeric backbone. Since polymers suitable

for fuel cells must be thermally, mechanically, and chemically stable at temperatures $\geq 80^\circ\text{C}$, non-fluorinated polymers are generally made up of polyaromatic or polyheterocyclic units, such as polysulfones, poly(ether sulfone)s, poly(ether ketone)s, poly(phenylquinoxaline), polybenzimidazole, and polyimides (Roziere and Jones 2003). Polyarylenes are high-temperature rigid polymers, with high Tg values, due to the presence of inflexible and bulky aromatic groups; they are cheap and commercially available and their structure allows the introduction of protogenic groups in order to get proton conduction properties (Smitha et al. 2005). Proton-conducting membranes can be obtained from thermostable non-fluorinated polymers through the following approaches (Roziere and Jones 2003):

- (i) Direct sulfonation of the polymer backbone (poly (aryl ether sulfone)s, poly(aryl ether ketone)s, polyphosphazenes, polyimides). Sulfonating agents such as fuming sulfuric acid, chlorosulfonic acid, trimethylsilyl chlorosulfonate, and sulfur trioxide-triethyl phosphate complexes are commonly used. The sulfonation is carried out either in “bulk” sulfuric acid as solvent or in solutions of dichloromethane. The sulfonation degree is controlled by reaction time, temperature, and the polymer/sulfonating agent ratio. The main drawback is the difficulty to control the distribution of the sulfonic groups along the polymer chains and the possibility of cross-linking with formation of sulfone links between polymer chains.
- (ii) Direct synthesis from monomer building blocks. The combination of sulfonated and non-sulfonated monomers allows a better control of the sulfonation degree and the distribution of the ionogenic groups over the polymer chain.
- (iii) Chemical grafting of sulfonated functional groups to the polymer main chain (polysulfones, poly(ether ketone)s, polybenzimidazole) does not require sulfonated monomers and offers an easier route to introduce locally and densely sulfonated structures into the aromatic polymer backbone.

- (iv) Acid-base complexes. An example is polybenzimidazole/phosphoric acid, in which the proton conductivity is mainly affected by the acid doping level and temperature. Limitations of these systems are the leaching out of the free acid in the presence of liquid water and the poor mechanical properties at high acid doping levels.

Membranes based on sulfonated polymers are commonly prepared by casting polymer solutions, in polar aprotic solvents (NMP, DMF, DMAc, DMSO), on a flat substrate, followed by solvent evaporation and acidification treatment. In all types of sulfonic polyelectrolyte membranes, the acid groups tend to cluster into hydrophilic regions that are hydrated or solvated in the presence of water or water/methanol solutions and are responsible for the water and proton transport; the polymer backbone segregates into hydrophobic regions which provide morphological stability and prevent dissolution in water (Roziere and Jones 2003). The water uptake of sulfonated membranes increases with the water activity, temperature, and number of acid functionalities and affects proton conductivity and mechanical stability. In polyaromatic ionomers with randomly distributed sulfonic groups, the rigid polyaromatic backbone prevents the formation of well-connected hydrophilic channels, and these sulfonated polymers attain suitable conductivities at high ion-exchange capacities (meq of $-\text{SO}_3\text{H}$ groups per 1 g of dry membrane) and high water contents, which negatively affect their mechanical and water resistance (Wang et al. 2012). Polyaromatic block copolymers, with hydrophilic sulfonated polymer segments (forming an interconnected three-dimensional network) and hydrophobic non-sulfonated segments (having a reinforcing effect), should better prevent excessive swelling in water, enhancing mechanical properties and assuring a good proton conductivity (Higashihara et al. 2009; Kim et al. 2004). Polyaromatic ionomers exhibit a methanol permeability lower than that of perfluorosulfonic acid membranes, so that they result particularly suitable for applications in direct methanol fuel cells (Xue and Yin 2006).

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Nonlinear Programming

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Problems of nonlinear programming (NLP) arise in many engineering applications. These involve (complex) process simulations, optimal experiment design for estimation of parameters, parameter estimation, optimal process design, optimal process control, and so on. In general, constrained NLP problems can be mathematically stated as (Bertsekas 1999)

$$\min_x f(x) \quad (1a)$$

$$\text{s.t. } \mathbf{g}(\mathbf{x}) \leq 0 \quad (1b)$$

$$\mathbf{h}(\mathbf{x}) = 0 \quad (1c)$$

where $\mathbf{x}$ represents vector of optimization (decision) variables, $f(\mathbf{x})$ is optimization criterion, and $\mathbf{g}(\mathbf{x})$ and $\mathbf{h}(\mathbf{x})$ stand for sets of inequality and equality constraints, respectively.

If the instance of problem (1a) does not involve (1b) and (1c), then the problem is referred to as unconstrained. Minimizer x^* must satisfy the following property (Boyd and Vandenberghe 2004)

$$\nabla f(x^*) = 0$$

and thus the problem boils down to solving the set of nonlinear equations. For solving this type of problems, one may use well-established algorithms such as steepest descent method and Newton or quasi-Newton methods.

However, in practice, any optimization problem involves constraints naturally. To treat constrained NLPs analytically, one may exploit Karush-Kuhn-Tucker (KKT) conditions which are based on the theory of Lagrange multipliers (Bazaraa et al. 1993). For practical purposes, one usually relies on using numerical methods. These are based on approximation of original problems into an unconstrained form (penalty, barrier, and interior point methods) or generating sequences of simpler but closely related subproblems (SQP and active set methods).

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Nonlinear Regression: Levenberg-Marquardt Method

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Nonlinear regression (Levenberg-Marquardt method). In almost every discipline of science and engineering, people encounter problem of parameters estimation of nonlinear models.

Among different available methods, Levenberg-Marquardt is a popular method to solve nonlinear least-squares problems effectively due to its ability to converge from a wide range of initial guess values of parameters (Davis 1993). An objective of nonlinear least-squares problem is to minimize the difference between a set of experimental data and the data generated by a model function. Given a set of experimentally observed data (x_i, y_i) , optimize the parameter θ of model function $f(x_i, \theta)$ to minimize the sum of the squares of the deviations. The objective function of least-squares problem is then formulated as

$$F(\theta) = \frac{1}{2} \sum_{i=1}^n r_i^2(x) \quad (1)$$

where n is the number of data points considered, $r_i(x) = f(x_i, \theta) - y_i$ is called a residual, and y_i is y component of the data point at x_i . If the function is a nonlinear in the model parameters vector $\theta = [\theta_1, \theta_2, \dots, \theta_m]^T$, where m is the number of parameters, then minimization of the objective function is carried out iteratively. The Levenberg-Marquardt algorithm starts with an initial guess for the parameters vector θ . In each iteration step, perturbation $\delta\theta$ of parameters is calculated and next iteration proceeds with a new estimate, $\theta + \delta\theta$. Levenberg (1944) proposed algorithm with the following search scheme to update the parameter:

$$(J_K^T J_K + \lambda I) \delta\theta_k = -J_K^T r_k \quad (2)$$

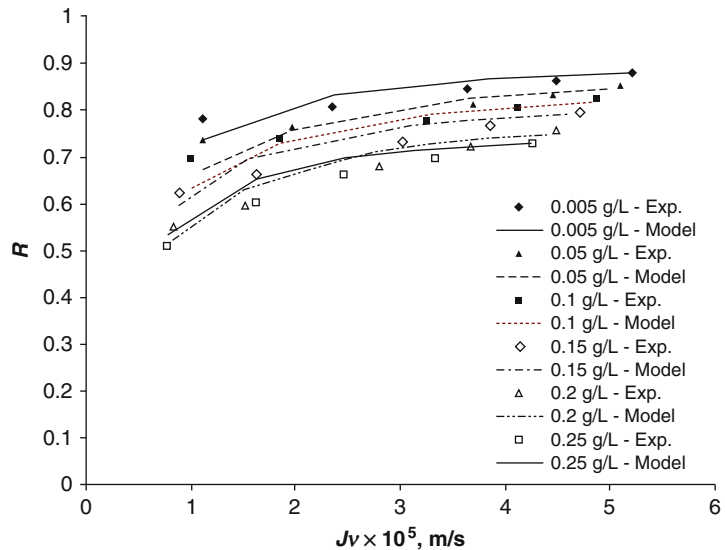
where I is the identity matrix, $\delta\theta$ is the perturbation to the estimated parameters, J is Jacobian matrix of residuals, and λ is a damping factor. Marquardt (Marquardt 1963) suggested update relationship by replacing the identity matrix I , with the diagonal of $J^T J$ resulting into Levenberg-Marquardt algorithm:

$$(J_K^T J_K + \lambda \text{diag}(J_K^T J_K)) \delta\theta_k = -J_K^T r_k \quad (3a)$$

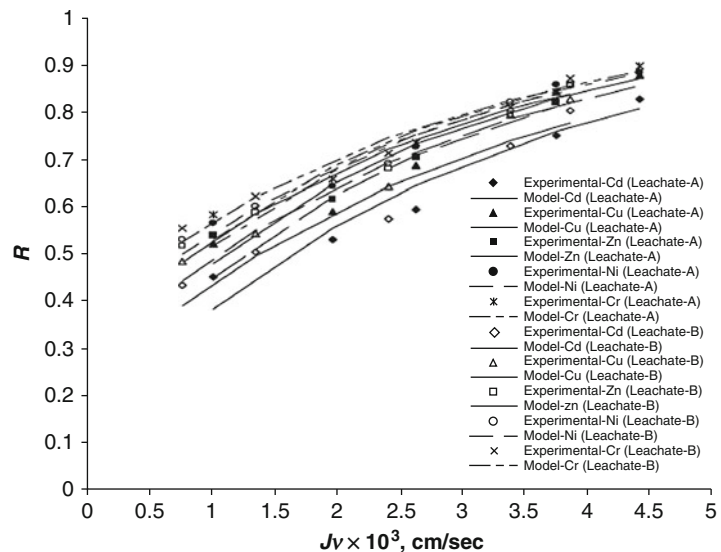
$$\theta^{k+1} = \theta^k + \delta\theta^k \quad (3b)$$

Levenberg-Marquardt method is considered to be a blend of steepest descent and Gauss-Newton

Nonlinear Regression: Levenberg-Marquardt Method, Fig. 1 Plot of true rejection (R) vs. permeate flux (J_v) and its comparison with the values calculated using irreversible thermodynamics model for the CdCl_2 – NiCl_2 –water system at different feed concentrations and feed flow rate of 10 L/min (Reproduced with permission from Elsevier)



Nonlinear Regression: Levenberg-Marquardt Method, Fig. 2 Comparison between experimental and estimated rejection rates of Cr^{3+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , and Cd^{2+} in leachate – A and B as a function of permeate volume flux by using ion transport model (feed flow rate = 5 L/min) (Reproduced with permission from Elsevier)



methods. It takes on a search direction like the steepest descent when the solution is far from a minimum. However, as solution gets closer to optimum, it behaves like that of Newton's method (Marquardt 1963; Le et al. 2012). The main steps involved in Levenberg-Marquardt method are summarized below (Le et al. 2012): (1) starting with an initial guess value of $\theta = \theta^0$ at $k = 0$; (2) specify modest value of $\lambda = \lambda_0$, $\lambda > 0$; (3) at the k th iteration, calculate $F(\theta^k)$; (4) solve equation (3) for θ^{k+1} and evaluate $F(\theta^{k+1})$; (5) if $F(\theta^{k+1})$

$> F(\theta^k)$, increase λ by a factor 10 and go to the step (4); (6) if $F(\theta^{k+1}) < F(\theta^k)$, decrease λ by a factor 10 and go to step (4); and (7) stop when trial solution met desired convergence criteria.

Levenberg-Marquardt method has been used extensively in the membrane separation processes to find membrane transport parameters and characteristics of the membrane using different membrane transport models. Chaudhari and Murthy (2010a, b), and Murthy and Chaudhari (2009a, b) used Levenberg-Marquardt method to determine

nanofiltration (NF) membrane transport parameters and then used those parameters to predict the performance of the membrane in the rejection of various metal ions from different solutions. Figure 1 (Chaudhari and Murthy 2010a) and Fig. 2 (Chaudhari and Murthy 2010b) show some of the results obtained using the Levenberg-Marquardt method. Some modified versions of Levenberg-Marquardt method were also used in membrane separation processes (Soltanieh and Gill 1981; Murthy and Gupta 1997, 1999).

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Nonsolvent Induced Phase Separation Process (NIPS) for Membrane Preparation

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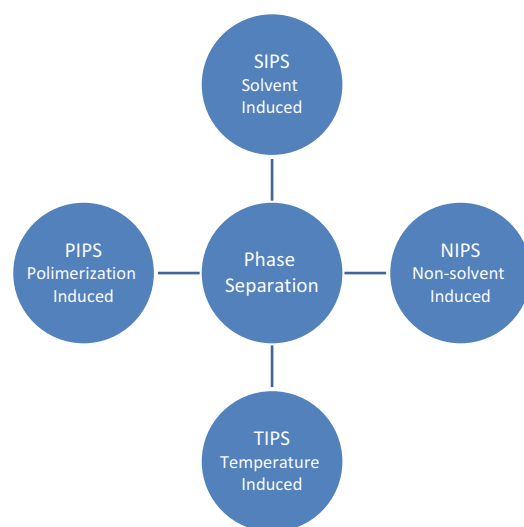
Synonyms

NIPS

Non-solvent induced phase separation process (NIPS) for membrane preparation.

Phase separation processes, in which a solid phase separates from a polymer solution, are the basis for the preparation of all kind of membranes. A scheme of these processes is reported in Fig. 1.

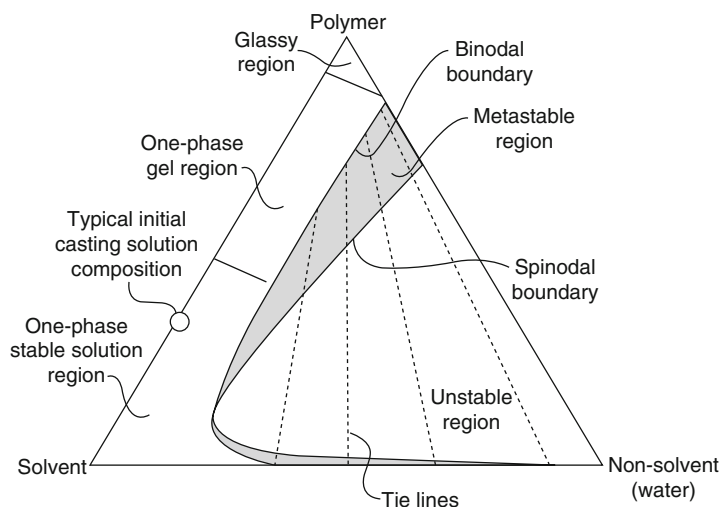
Among them, the *non-solvent induced phase separation* (NIPS) is the most commonly used thanks to its versatility and to the possibility of preparing a great variety of membranes (Mulder 1996). According to this process, the polymer solution is immersed in a non-solvent bath



Nonsolvent Induced Phase Separation Process (NIPS) for Membrane Preparation, Fig. 1 Scheme of the phase separation processes

Nonsolvent Induced Phase Separation Process (NIPS) for Membrane Preparation,
Fig. 2 Phase diagram of a three-component system

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(coagulation bath), typically water, where the exchange of solvent and non-solvent takes place: the solvent migrates from the polymer solution to the coagulation bath, while the non-solvent follows the reverse path, leading to the formation of the membrane. As raw material, many polymers can be used, provided that they are soluble in a solvent or in a mixture of solvents. Membranes both in *flat* and *tubular* conformation can be realized. In the first case, the polymer solution is cast on a support, typically a nonwoven polyester or a glass plate (Baker 2004), by means of a *casting knife* before dipping into the coagulation bath. The most important parameters affecting the structure of the resulting membrane are the composition of the coagulation bath, the composition of the casting solution, the exposure time, the humidity, and the temperature of the air. Also the thickness of the casting solution, generally adjusted in the range from few tens to some hundreds of microns, plays an important role in determining membrane characteristics.

In the case of the tubular conformation, the polymer solution and the *bore fluid* are co-extruded through a *spinneret* giving rise to a self-supporting structure which, depending on the diameter, is classified as *hollow fiber* (diameter below 0.5 mm) or *capillary* membrane (diameter between 0.5 and 5 mm). In addition to the parameters that affect the structure and the performance of flat membranes, in the case of tubular

conformation, the following must be considered: *viscosity* and extrusion rate of the polymer solution, composition and feeding rate of the bore fluid, *air gap* distance, and dimensions of the spinneret.

Some important aspects concerning NIPS, such as the exchange rate of solvent and non-solvent and the velocity of the phase separation, are related to *kinetics* and strongly influence the morphology of the membrane. However, also *thermodynamics* plays a relevant role in phase separation processes. Interactions among polymer, solvent, and non-solvent can be discussed in terms of *free energy* of mixing (ΔG_m) and are described in the *solubility parameter theory*. The thermodynamic stability of three-component mixture (polymer, solvent, and non-solvent) is graphically described by a *ternary phase diagram* (Fig. 2).

The corners of the triangle represent the pure components and the sides are binary mixtures. Points within the triangle represent ternary mixtures. Three regions can be distinguished separated by *binodal* and *spinodal* boundary: the region on the left of the binodal boundary represents the *one-phase* thermodynamically stable region, in turn subdivided in *solution*, *gel* and *glassy* region; between the binodal and spinodal boundary, a *metastable* region, thermodynamically unstable in which no phase separation occurs; and on the right of the spinodal boundary,

a thermodynamically unstable region where phase separation occurs. The polymer solution spontaneously separates into a polymer-rich phase and a polymer-poor phase whose compositions are given by the intercepts of the *tie line* with the binodal boundary.

The formation of membranes by NIPS can be summarized as follows:

- The polymer solution comes in contact with the non-solvent and the exchange of solvent and non-solvent begins.
- As the polymer solution loses solvent and enriches of non-solvent, the composition enters the two-phase region; polymer precipitation occurs giving rise to the formation of a polymer-rich phase and a polymer-poor phase.
- The exchange of solvent and non-solvent proceeds, the composition of the polymer-rich phase moves toward the polymer/non-solvent side, and the membrane is formed.

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NOx Effect on Membrane Properties

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Combustion of fossil fuels at high temperature in air results in the generation of nitrogen oxides, commonly and collectively referred to as NOx. This mixture is dominated by NO and to a lesser extent NO₂, but can also consist of higher nitrogen oxides, such as N₂O₄, but only rarely includes N₂O. The generation of NOx is the result of partial oxidation of N₂ in combustion, as well as nitrogen associated with the fuel. Dependent on the fuel

type and combustion temperature, NOx can exist in the flue gas on the order of 10–500 ppm. Their emission is heavily regulated and must be reduced to 2–5 ppm before flue gas can be vented to the atmosphere. This has implications in flue gas desulfurization and CO₂ postcombustion capture from flue gas.

The effect of NOx on membranes is a sparsely studied area, with the permeability, selectivity, and effects of NO and NO₂ on polymeric membranes relatively unknown. Information on performance must be extrapolated from known properties, such as kinetic diameter and solubility.

NO has a smaller kinetic diameter than most gases found in flue gas, such as N₂, O₂, and CO₂. Hence, molecular sieve-based membranes will show selectivity for NO relative to these gases. Conversely, NO₂ has a larger kinetic diameter than other gases present in flue gas and will be retained in the retentate. For nonporous membranes where solubility is an important factor, it is expected that membranes show selectivity for NO₂ compared to NO, given the difference in critical temperature.

For CO₂-selective membranes for carbon capture from flue gas, nonporous polymeric membranes will display CO₂/NO selectivity because of strong CO₂ solubility. This has been observed for the glassy polymeric membranes of polysulfone, and the polyimides Matrimid 5218 and 6FDA-TMPDA (Table 1; Scholes et al. 2009). Conversely, NO₂ will have a greater permeability than CO₂ in nonporous membranes because of strong NO₂ solubility, and this has been reported for poly tetrafluoroethylene (PTFE), with a permeability of 15.9 barrer and a NO₂/CO₂ selectivity of 1.6 (Pasternak et al. 1970).

The plasticization and aging effects of NOx on membranes has not been reported in the literature to date. In the presence of water, NOx readily forms nitric acid, and this will degrade membrane

NOx Effect on Membrane Properties, Table 1 NO permeability (barrer) through glassy polymeric membranes

	Polysulfone	Matrimid 5218	6FDA-TMPDA
NO permeability (barrer)	3.1 ± 0.6	3.7 ± 0.6	168 ± 16

materials over time. Hence, in the humid environment of flue gas it is expected that NO_x will have similar degradation performance on membranes as those observed for SO_x.

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Nuclear Science and Technology, Membrane in

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Recent achievements in the area of membrane processes are being applied for solving the problems in nuclear science and technology. The most important application of membrane processes is the treatment of liquid radioactive waste, often combined with the recovery of valuable materials such as water, boric acid, metals, or radioactive isotope of hydrogen – tritium. Separation of stable isotopes and enrichment of uranium in the ²³⁵U isotope for production of nuclear fuel, as well as cleaning the exhaust gas from nuclear power plants, are possible with membrane processes. Reverse osmosis may be applied in nuclear desalination; other membrane processes, like membrane distillation, are also considered as an alternative to energy-intensive distillation methods.

Separation of Isotopes

The issue of membrane in isotope separation (► [membrane for the isotope separation](#)) is

discussed in the scientific literature from the first application of molecular diffusion for enrichment of uranium in its less abundant ²³⁵U isotope for military purposes during the Second World War. The method is still applied in several installations producing the enriched uranium for nuclear fuel for power reactors. The studies on separation of isotopes of other elements like hydrogen, oxygen, nitrogen, carbon, lithium, chlorine, and lanthanides, by using different membrane processes are carried out in many laboratories.

Radioactive Waste Treatment

The application of membrane processes for radioactive waste treatment (Membranes in nuclear waste treatment) is a common industrial practice. Nuclear waste processing by pressure-driven membrane processes (nuclear waste processing by pressure-driven membrane processes) is a standard method applied in nuclear power plants and nuclear centers; thermal membrane process (nuclear waste processing by thermal processes), namely, membrane distillation, was proposed for liquid low and intermediate waste concentration. Advanced researches are carried out to employ liquid membranes for processing radioactive waste, especially the waste from the back-end of nuclear fuel cycle. Membrane contactors pose new field of applications including such techniques like supported liquid membranes (nuclear waste processing by supported liquid membranes) and membrane liquid–liquid extraction.

Separation of Tritium

Tritium is emitted by nuclear reactors and fuel reprocessing plants in gaseous and liquid (HTO) forms. The studies on application of polymeric membranes for both gaseous tritium and tritiated water separations are carried out in many laboratories. For separation of HTO, the membranes from poly[bis(phenoxy)phosphazene] and carboxylated derivatives were used (Duncan and Nelson 1999). Membranes made from regenerated cellulose, polysulfone, and

polytetrafluoroethylene were also tested for this purpose. Separation factors $\alpha_{\text{H}_2\text{O}/\text{HTO}}$ in membrane process were not higher than 1.04 for cellulose and 1.02 for polysulfone, while for PTFE membranes were as high as 1.06–1.22 (Zakrzewska-Trznadel 2006).

Recently published papers cover the application of polymeric gas separation (GS) membranes for recovery of tritium compounds (HT, HTO) (Le Digabel et al. 2003; Iwai et al. 1999; Ishida et al. 2000). Such membranes like those manufactured from glassy and amorphous polymers, mainly polyimide and polycarbonate, as well as polyphenylene oxide, assembled in modules (e.g., Mc Generon Inc., type B210, Ube Industries, Ltd. Type NM-B05A, Parker, type 2112-NX-1-300) were considered.

The works performed on hydrogen isotope separation by permeation methods concern nuclear reactor safety and thus release of tritium from nuclear water reactors and fuel reprocessing plants. On the other hand, a lot of space is devoted to researches on the security of the fuel cycle for future fusion reactors (Basile et al. 1995). Various systems are proposed: palladium alloy-based separators, catalytic systems with metallic membranes, integrated systems with ceramic catalytic reactors, and electrolytic reactors.

Separation of Radioactive Gases

Apart from separation of tritium from radioactive gaseous waste produced by nuclear reactors, the other pollutants like noble gases may be separated by membrane methods. In recent years, the works showing the interest in membrane separation processes of noble gases (Nörenberg et al. 2001) were published. Membranes used for this purpose were polyimide hollow fibers and flat-sheet filters made from polyethylene terephthalate (PET) or oriented polypropylene. The methods for selective separation of tritium from the gases released from nuclear facilities have been studied primarily in the context of measuring the emission of this isotope (Sasaki et al. 2003).

Membrane Methods for Nuclear Desalination

Because seawater desalination is energy intensive, the use of energy from nuclear reactors for desalination systems seems to be justified. In some cases membrane processes can be competitive with thermal methods like multistage flash evaporation, multiple effect distillation, or vapor compression. There are several examples of application of RO in such nuclear reactor-desalting systems (IAEA Technical Reports Series 2000; Kim et al. 2002). The employment of membrane distillation to produce desalted water with nuclear energy was also considered (Khayet et al. 2006).

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Nuclear Track Filters

► [Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices](#)

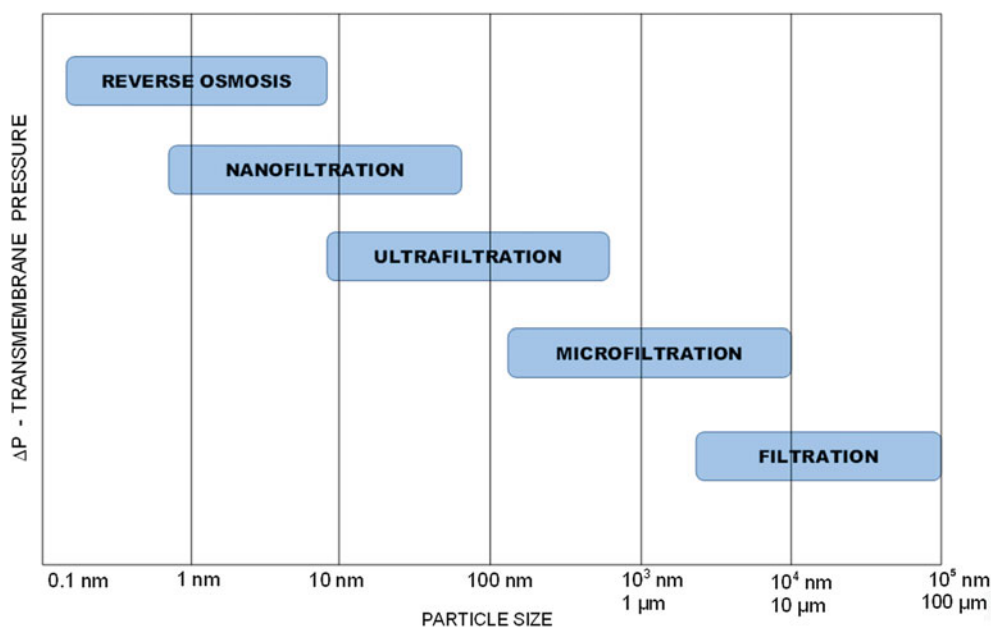
Nuclear Waste Processing: Pressure-Driven Membrane Processes

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The pressure-driven membrane processes such as reverse osmosis (RO), nanofiltration

(NF), ultrafiltration (UF), and microfiltration (MF) are the most commonly used membrane methods of radioactive waste processing. The reasons for a wide use of membrane methods are numerous: they are mature technologies with long design and operation experience, well proven in nuclear industry, with broad spectrum of membranes and membrane modules developed. The variety of pressure-driven membrane processes covers wide spectrum of media: from ionic species to large particles (Fig. 1). Therefore, they are suitable for large number of applications, being flexible in process configurations and system optimization. They can be easily integrated with other conventional methods to form efficient treatment systems. Pressure-driven membrane processes are especially convenient for the concentration of large volumes of low and intermediate level radioactive waste with low salinity and low radioactive species content.

Reverse osmosis, well-developed technology, has found many applications in nuclear industry. It is used for removal of radionuclides from various streams in nuclear power plants: reactor coolant, floor drains, reactor outage waste, spent resin



Nuclear Waste Processing: Pressure-Driven Membrane Processes, Fig. 1 Pressure-driven membrane processes – range of application

Nuclear Waste Processing: Pressure-Driven Membrane Processes, Fig. 2 Three-stage RO plant for the treatment of institutional radioactive waste at Radioactive Waste Management Plant at Swierk, Poland



sluice water, the waste from steam generator chemical cleaning, and fuel cooling pond water. It can be applied for the liquid waste from research activities and medical applications (Fig. 2), as well as for cleaning the defense and reprocessing effluents (IAEA Technical Reports Series 2004). Since RO rejects all dissolved matters from water solution, the product from RO modules – high-purity water – may be recycled within the nuclear power plant. Big variety of RO systems is available in the market and various polymeric materials are used for membrane manufacturing.

Nanofiltration is able to separate monovalent ions from multivalent ions or organic compounds from monovalent ions. The best known application of NF is boric acid recovery from reactor cooling water (Zakrzewska-Trznadel 2008). NF can be applied for removal of dissolved uranium ions from wash solutions discharged from fuel fabrication plants. Integrated with macromolecular ligands, NF was applied for separation of lanthanides and actinides (Chitry et al. 2001a) and separation of neodymium and gadolinium isotopes (Chitry et al. 2001b).

Ultrafiltration is a good pretreatment method before reverse osmosis. It is used for removal of colloid matters and particles to avoid the fouling of RO membranes, as well as alpha-emitting substances, namely, actinides, which are often in colloidal form. Combined with chelating compounds or dispersed sorbents that bind small ions, UF can be applied for removal of dissolved radioactive metal ions from diluted aqueous solutions. UF membranes reject complexed or sorbed ions

allowing uncomplexed ions to pass through as permeate. Ultrafiltration may be employed for the treatment of water from fuel storage ponds, cleaning the laundry wastes, solvent wash liquors, and plutonium evaporator overheads from reprocessing lines or purification of effluents from fuel fabrication plants. The decontamination factors reported in the literature are in the range of 1000 for α emitters and 100 for β and γ species, and the overall volume reduction of the order of 10^4 is achieved with UF systems. Inorganic, ceramic membranes in the region of UF pore size are offered in the market, which enhance the potential of the process.

Microfiltration is applied as a pretreatment stage before RO or UF; it can be also used separately for the concentration of radioactive suspensions and dewatering of concentrated sludge. It may be applied with conjunction of precipitation process to remove various kinds of radionuclides. Both polymeric and inorganic membranes are employed for MF process.

In spite of intensive studies in the field of membrane technologies and continuous development of novel processes, the pressure-driven membrane processes remain the leading membrane methods in nuclear industry Zakrzewska-Kołtuniewicz (2015).

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Nuclear Waste Processing: Supported Liquid Membranes

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Supported liquid membranes (SLM), also called immobilized liquid membranes, have found a number of applications in nuclear industry – from uranium mining to reprocessing of spent nuclear fuel. In supported liquid membrane, two phases, feed and receiving solutions, are separated by porous barrier with organic phase inside the pores. In order to increase the mass transport rate between the phases, the carrier, which forms complex with one of the separated

species, is introduced to the organic phase. Such a facilitated transport causes not only fast transport rates but also results in higher selectivity of the process.

SLM were studied for radioactive waste treatment and for removal of actinides and fission products from the waste after reprocessing of nuclear fuel. Radionuclides, such as cesium, strontium, cerium, and europium, were separated from radioactive solutions to reduce the radiotoxicity of the waste. Uranium plutonium and americium removal from the wastes produced in the back-end of fuel cycle, as well as the effective methods for actinides partitioning, were broadly described in the literature. Example applications are collected in the Table 1.

The main drawback of immobilized liquid membranes is their low stability associated with loss of extractant via volatilization or dissolution into contacting phase (Kołodziej and Drioli 2008). The advantages are high selectivity of the method allowing a wide range of applications and easy optimization of the membrane-extractant system. Although the industrial application of this process is far from implementation, ongoing research on new extracting agents for actinides takes place in many laboratories around the world. A solution to the problem of loss of extracting agent may be development of inclusion membranes. Polymer inclusion membranes (PIM) in some cases incorporate base polymer and a suitable extractant, while in other cases a plasticizer may be needed to be added (Bayou et al. 2010). PIM have been successfully developed for extraction of radionuclides from radioactive waste using various extracting agents like TOPO, Cyanex 272, Cyanex 301, Cyanex 302, CMPO, TODGA, D2EHPA, and crown ethers (Kusumocahyo et al. 2004; Kozłowski et al. 2006; Bhattacharyya et al. 2011). Another approach for the extraction of radionuclides with selective organic reagents is application of membrane solvent extraction carried out in membrane contactors (Drioli et al. 2005).

Nuclear Waste Processing: Supported Liquid Membranes, Table 1 Supported liquid membranes for treatment of radioactive waste

Separated radionuclides	Application	Extracting agent (LM)	Stripping solution	Support	Reference
Pu(IV)	Separation of plutonium from radioactive waste	Tri-n-butyl phosphate (TBP)	0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 3 M HNO_3	Hollow fiber polypropylene (Enka) membrane	Rathore et al. 2001
Pu(IV)	Separation of plutonium from radioactive waste	2-ethylhexyl 2-ethylhexyl phosphonic acid in n-dodecane	0.05 M HNO_3 and 0.3 oxalic acid solution	Polypropylene Enka 2E HF-PP membrane	Kedari et al. 1999
U(VI) ^{233}U ,	Recovery of uranium from 6 M HCl at the back-end of fuel cycle	Alamine 336 in toluene	Distilled water	PTFE flat sheet membrane	Lakshmi et al. 2004
^{232}Th	U/Th separation in 4 M HNO_3 in the presence of ^{137}Cs , $^{85,89}\text{Sr}$, and ^{59}Fe	N,N-di(2-ethylhexyl) isobutyramide (D2EHIBA) in n-dodecane	0.01 M HNO_3	PTFE flat sheet membranes, 0.45 μm , 72 % porosity (Sartorius)	Shailesh et al. 2006
U(VI)	Actinides partitioning	N,N,N',N'-tetra-2-ethylhexyl-3-pentane-diamide (T2EHDGA) in n-dodecane, 30 % iso-decanol as the modifier	0.01 M HNO_3	PTFE flat sheet membranes, 0.45 μm , 64 % porosity	Panja et al. 2011
U(VI)	Recovery of actinides at the back-end of fuel cycle from acidic feeds	Tetraoctyldiglycolamide (TODGA) in n-dodecane	0.1 M HNO_3	PTFE flat sheet membranes	Panja et al. 2009
U(VI)	Recovery of actinides at the back-end of fuel cycle from acidic feeds	N,N,N',N'-tetra-2-ethylhexyl-3-pentane-diamide (T2EHDGA) in n-dodecane, 30 % iso-decanol as the modifier	0.01 M HNO_3	PTFE flat sheet membranes	Panja et al. 2012
U(VI)	Extracting of uranyl ions from 6 M HCl environment	Aliquat 336 (N-methyl-N,N-diocetyl octan-1-ammonium chloride)	Distilled water	PTFE flat sheet membranes (Sartorius)	Mohapatra et al. 2006
U(VI)	Recovery of uranium from nitrate media	TBP in kerosene	NaOH	Hollow fiber membrane contactor	Ramkul et al. 2007
U(VI)	Separation of uranium from phosphoric acid	Tri-n-octylphosphine oxide (TOPO) in n-dodecane	Ammonium carbonate	PTFE flat sheet membranes, 0.45 μm , 84 % porosity	Singh et al. 2007
Am(III)	Extraction Am (III) from 1–6 M HNO_3	TEHDGA in dodecane	0.1 M HNO_3	PTFE flat sheet membranes (Sartorius) 0.20–5 μm	Panja et al. 2008

(continued)

Nuclear Waste Processing: Supported Liquid Membranes, Table 1 (continued)

Separated radionuclides	Application	Extracting agent (LM)	Stripping solution	Support	Reference
Am(III)/Nd (III)	Separation of Am ³⁺ from 3 M HNO ₃ and from simulated high-level waste (SHLW) solution	<i>N,N,N',N'</i> -tetraoctyl diglycolamide (TODGA) and <i>N,N</i> -di- <i>n</i> -hexyl octanamide (DHOA) as a modifier in normal paraffin hydrocarbon (NPH) as the carrier solvent	Distilled water	Polypropylene membrane 2.5 × 8 Liqui-Cel [®] Extra-Flow hollow fiber module (Celgard)	Ansari et al. 2008
Am/Eu	Separation of actinides and lanthanides	Bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301)	0.1 M H ₂ SO ₄	PTFE membrane (Fluoropore, FP 045 Sumitomo Electric Ind.), 0.45 μm, 74 % porosity	Hoshi et al. 2000
La, Ce	Selective separation of La (III) from Ce(IV)	Tri- <i>n</i> -octylamine (TOA) in kerosene	0.25 M Na ₂ CO ₃	Hollow fiber (Hoechst Celanese Charlotte, NC Liqui-Cel [®] Extra-Flow module, Celgard with PTFE membranes)	Ura et al. 2005
Ce(III)	Separation of Ce (III) from fission products during PUREX process (9 M HNO ₃ , 2 M NaBrO ₃)	Tri- <i>n</i> -butylphosphate (TBP) in kerosene	1 M HNO ₃	Cellulose nitrate flat sheet membrane (Sartorius), 0.2 μm, porosity 70 %	El-Said et al. 2002
Ce(III)	Separation of cerium from low-level radioactive waste	CMPO; TBP as a modifier, in dodecane	Aq. solutions of trisodium citrate and disodium citrate	Plate-and-frame module	Teramoto et al. 2000
Sc, Zr, Nb, Hf, Ce, Pm, Gd, Yb, Lu	Permeation of rare earth elements in SLM	Bis(2-ethylhexyl) hydrogen phosphate in decalin	0.75, 1.0, 2.3 and 4.0 M HCl	PTFE flat sheet	Ambe et al. 1998
Cs	Separation of cesium from fission products of irradiated uranium	Di- <i>t</i> -butyl benzo 18 crown 6 carrier	Distilled water	Polypropylene membrane	Mohapatra et al. 2004
Cs	Selective extraction of cesium ion from aqueous solutions	1,3-Dipropylloxycalix[4] arene crown ether (CCE1) and 1,3-dipropylloxycalix[4] arene dibenzo crown ether (CCE2) in chloroform	Deionized water	Polypropylene, Celgard 2400 (Hoechst Celanese Co.), pore size: 0.04 μm × 0.12 μm, 41 % porosity	Kim et al. 2001
Cs	Separation of cesium in 3 M HNO ₃	Calix-[4]-bis (2,3-naphtho)-crown-6 as carrier in (2-nitrophenyloctyl) ether and <i>n</i> -dodecane	Distilled water	Hollow fiber module	Kandwal et al. 2011a

(continued)

Nuclear Waste Processing: Supported Liquid Membranes, Table 1 (continued)

Separated radionuclides	Application	Extracting agent (LM)	Stripping solution	Support	Reference
Cs	Separation of cesium from other radionuclides in multicomponent nitric acid solution	Chlorinated cobalt dicarbollide (CCD) in phenyl trifluoromethyl sulfone (PTMS)	8 M HNO ₃	Impregnated PTFE flat sheet membranes, 0.45 µm, 72 % porosity (Sartorius)	Mohapatra et al. 2010
Cs	Recovery of cesium from pressurized heavy water reactor (PHWR) simulated high-level waste (SHLW)	Calix[4]arene-bis(2,3-naphtho)crown-6	Distilled water, NaOH neutralization	Polypropylene hollow fiber	Kandwal et al. 2011b
Sr	Selective removal of Sr ²⁺ from aqueous nitrate medium	4,4'(5')di-tert-butyl-dicyclohexano-18-crown-6 (DtBuCH18C6) in 1-octanol	Distilled water	PTFE flat sheets, pore size: 0.45 µm	Rawet et al. 2006
Sr	Selective Sr separation from pressurized heavy water reactor simulated high-level waste (SHLW)	Di-tert-butyl-dicyclohexano-18-crown-6 (DTBCH18C6) dissolved in a mixture of 80 % 2-nitrophenyl ether and 20 % n-dodecane	Distilled water	PTFE membrane	Raut et al. 2012
Sr	Separation of strontium from 3 M HNO ₃	4,4' (5')di-tert- butyl-dicyclohexano-18-crown-6 (DTBCH18C6)	Distilled water, NaOH neutralization	Hollow fiber membranes	Kandwal et al. 2012
Sr/Y	⁹⁰ Y separation from its parent ⁹⁰ Sr in 0.1 MHNO ₃ for generator production	Bis-(2-ethylhexy) phosphate (HDEHP), tributylphosphate (TBP)	3 M HNO ₃	Nuclear track microfilters	Happel et al. 2003
⁹⁰ Y	Yttrium separation from high-level waste for application for nuclear medicine	2-ethylhexyl-2-ethylhexyl phosphonic acid (KSM017 equivalent to PC 88A)	0.5 M HNO ₃ or 0.5 M HCl	PTFE membranes	Ramanujam et al. 2001
Tc	Removal of Tc (VII) from water and concentrated alkaline solutions	2-nitrophenyl octyl ether (NPOE)	1.5 M HNO ₃	Flat sheet polymeric membranes	Chen et al. 2001
Tc	Separation of ^{99m} Tc from ⁹⁹ Mo	Tri-octyl phosphine oxide (TOPO) in kerosene	0.9 % NaCl	Celgard-2400 polypropylene film, 0.02 µm, 38 % porosity	Yassine 2000
Co	Separation of cobalt ions from water solutions	2-ethylhexyl hydrogen 2-ethylhexyl phosphonate HEH(EHP) in kerosene	H ₂ SO ₄	PTFE filters (Millipore Co., 0.50 µm, 85 % porosity)	Youn et al. 1995

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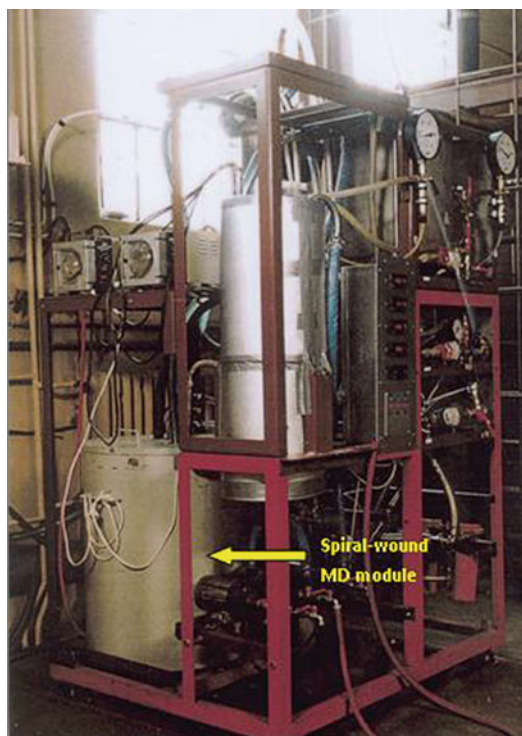
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Nuclear Waste Processing: Thermal Processes

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Despite many potential benefits posed by membrane distillation (MD), the scale of applications

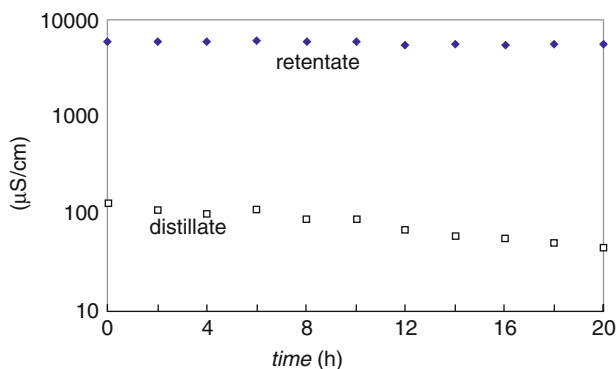


Nuclear Waste Processing: Thermal Processes, Fig. 1 Pilot plant for liquid radioactive waste concentration at Institute of Nuclear Chemistry and Technology, Warsaw

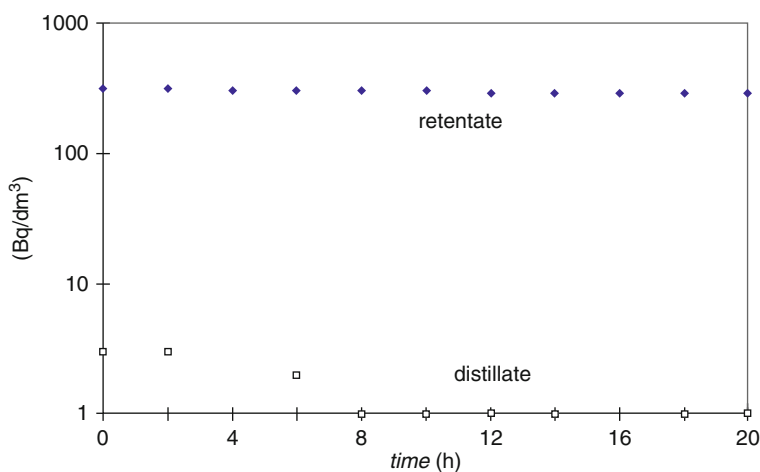
of this process is still limited. Temperature gradient-driven membrane processes were developed for concentrating liquid radioactive waste from institutional applications (Chmielewski et al. 2000; Fig. 1).

As the MD process is characterized by high retention of nonvolatile solutes, large decontamination factors are expected for radionuclides, which are present in liquid radioactive effluents in mainly ionic form. The process was tested in laboratory scale and in the pilot plant. High decontamination was achieved for radionuclides, such as ^{192}Ir , ^{170}Tm , ^{140}La , ^{134}Cs , ^{133}Ba , $^{192\text{m}}\text{In}$, $^{110\text{m}}\text{Ag}$, and ^{65}Zn , which were completely retained by the membrane, as well as for ^{137}Cs and ^{60}Co , which were predominant components of institutional radioactive waste. The decontamination factors for these radionuclides were 44 and 4,336, respectively (Zakrzewska-Trznadel et al. 1999). In the closed-loop membrane

Nuclear Waste Processing: Thermal Processes, Fig. 2 Specific conductivity of retentate and distillate vs. time during the concentration of radioactive waste



Nuclear Waste Processing: Thermal Processes, Fig. 3 Specific radioactivity of retentate and distillate vs. time during the concentration of radioactive waste



apparatus, the specific conductivity of the retentate does not change, while specific conductivity of distillate decreases (Fig. 2). In the same time, radioactivity of the retentate is also stable (however, small sorption in the unit is observed), and the radioactivity of distillate is on the natural background level (Fig. 3). The distillate produced by MD module is clean water, which can be reused in the nuclear plant.

The novel process of MD is advantageous, not only because of high decontamination factors and retention factors but also due to the simplicity of the apparatus applied and its ability to utilize waste heat from power sources such as nuclear reactors. The other advantages of MD are a possibility of running the process to high-solute concentrations, sufficient for direct immobilization of the waste, a high concentration in one-stage operations, elimination of high pressures, and reduction of sorption of radioactive species inside the

membrane pores since pores are filled with water vapor. MD can be easily integrated with other processes to form hybrid systems (Zakrzewska-Trznadel 2008). Membranes manufactured from PTFE, PP, or PVDF are used in the process. The average pore size of the membrane is 0.2–1.0 μm and the volume porosity is 70–80 %.

Different configurations were tested: shell-and-tube capillary, spiral-wound modules, and plate-and-frame systems with flat sheet membranes (Khayet et al. 2005). All arrangements of MD are possible to use: direct contact, air gap, sweep gas, and vacuum membrane distillation; however, the most convenient configuration for industrial applications, as well as this selected for radioactive waste processing, seems to be the direct contact MD.

Beneficial solution appears application of membrane distillation in nuclear desalination, both for radioactive waste treatment and to produce desalted

water (Khayet et al. 2006). Thermally driven process was also proposed for separation of light isotopes of hydrogen and oxygen for production of heavy water used in CANDU type reactors, and heavy-oxygen water for applications in nuclear medicine, i.e. PET examinations (Zakrzewska-Trznadel et al. 1996; Chmielewski et al. 2002).

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heterogeneous, surface-catalyzed nucleation (Cahn 1960). The nucleation stage can be surpassed when a seed material is used, on which crystallization can take place by addition of new atoms, ions, or polymers. This is typically applied in reactors for precipitation such as the pellet reactor for water softening. This is heterogeneous precipitation, for which a moderately supersaturated solution is needed (with stability index $SI = 1-2$). Heterogeneous precipitation is easier than homogeneous precipitation, since there is no need to create a new surface (and to supply the energy needed for this). This also allows a better control of the crystallization.

Homogeneous nucleation sets off with the creation of a small nucleus, which contains the newly forming crystal. This stage in the process is relatively slow, because the initial crystal components have to arrange in the correct orientation and position to adhere and form the crystal. Therefore, a larger oversaturation is needed ($SI = 3-4$). Once a nucleus is formed, crystals may grow more rapidly because they contain dislocations and other defects, which act as growth points and catalysts for structural transformation and long-range order formation (Frank 1949).

Nucleation stage crystal growth can be described by the self-consistent theory of nucleation (Girshick and Chiu 1990). According to the self-consistent theory, the Gibbs free energy ΔG needed for nucleation can be written as:

$$\Delta G = (4\pi r^2 - s)\sigma - (n - 1)k_B T \ln S$$

in which k_B is the Boltzmann constant, S is the supersaturation, and s is the surface area of a monomer. From this, the nucleation rate can be calculated as:

$$I_{SCT} = \frac{\exp\left(\frac{\sigma s}{k_B T}\right)}{S} I$$

in which I is the rate calculated from the classical nucleation theory. The exponential coefficient in the equation takes the surface energy of the monomer into account.

Nucleation Stage Crystal Growth

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Nucleation is the initial stage of crystal growth and can be either homogeneous nucleation or

Nucleation is an important phenomenon in membrane synthesis, mainly applied for synthesis of inorganic membranes. For example, Lin et al. (2001) prepared silicalite membranes by a single hydrothermal synthesis on nanoscale-silicalite-seeded porous tubular supports. An incompact crystal layer was obtained, especially on the unseeded support. Silicalite crystals preferentially grew onto the support tubes seeded with silicalite powders with size below 4 μm . The silicalite seed particles mainly provided nucleation sites (heterogeneous nucleation) and enhanced silicalite crystal growth in all directions onto the support, resulting in the formation of a thin and dense crystal layer.

For polymeric membranes, the nucleation stage is typically fast, and homogeneous nucleation is usually applied.

A direct application of nucleation for crystallization is encountered in membrane crystallization (Curcio et al. 2001). In a membrane crystallizer, a solution is concentrated by, e.g., membrane distillation, so that a supersaturated solution is obtained (Curcio and Drioli 2005). Subsequently, the supersaturated solution is crystallized in a second unit, which yields crystals with extraordinary purity. The process uses heterogeneous nucleation due to the presence of a membrane surface acting as growth points. Thus, the membrane is used as an active surface to promote heterogeneous nucleation, but also for mass transfer. This allows a good process control and fast crystallization; membrane-assisted crystallization is in that sense superior to other crystallization methods. For these reasons, membrane crystallization is a promising process not only for inorganic salts (Van der Bruggen et al. 2004) but also for proteins with substantial added value (Di Profio et al. 2003). A high uniformity in size was

obtained for crystallization of trypsins in a membrane crystallizer (Di Profio et al. 2005), with crystals produced in forced solution flow found to be more uniform than those obtained in a quiescent membrane system. The crystallization system was further optimized by increasing solution velocity to a maximum.

Cross-References

- [Membrane Crystallization \(MCR\)](#)
- [Membrane Distillation \(MD\)](#)

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O₂/N₂ Separation

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Separation of air into oxygen and nitrogen is an important process, and this separation process has been applied in an industrial scale such as oxygen (O₂) enrichment from air (medical devices) and nitrogen (N₂) enrichment from air (used as protecting atmosphere for oxygen-sensitive compounds) (Jeazet et al. 2012). There are three technologies that currently exist for separating oxygen and nitrogen from the air including cryogenic distillation, pressure swing adsorption (PSA), and membranes. Among these three technologies, cryogenic distillation is considered the most mature technology and allows for the production of both high purities (>99 %) and large-scale productions. However, this technology is renowned to be complex, expensive, and energy intensive, which consumes about 15 % of the electrical output of the power station (Hashim et al. 2011).

PSA is a technology that used to separate some gas species from a mixture of gases under pressure based on the molecular characteristics of the species and affinity for an adsorbent material. Under high pressure, gases tend to be attracted to solid

surfaces (adsorbed), and different gases tend to be attracted to different solid surfaces. For example, in air mixture, carbon molecular sieves (CMS) as the adsorbent bed will adsorb oxygen and water vapor molecules under high pressure while allowing N₂ gas to pass through. Rufford et al. (2012) claimed that the preferential adsorption of components from a gas mixture can be achieved by one, or a combination, of the following mechanisms:

1. Differences in the adsorbate-surface interactions and/or adsorbate packing interactions when the system reaches equilibrium
2. Differences in the size and/or shape of gas molecules
3. Differences in the diffusion rates of molecules through the adsorbent pores

Yet, the main disadvantage of PSA occurs when large flow rates of N₂ are needed; therefore, a large vessel needs to be utilized which consequently increased the installation cost.

The development of membranes for partial air separation progressed rapidly since the 1980s, and this technology is attractive compared to the conventional separation facilities because membrane-based devices are much smaller and can be operated at lower temperature. For dense polymeric membrane, the differences in solubility and diffusivity of O₂ and N₂ in and through the membrane materials will make the separation between the gases occurred. In solution-diffusion model,

permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. Polyimide, polycarbonate, polysulfone, polyethersulfone, and other aromatic polymers are commonly used as polymeric membrane-based devices for gas separation. Mixed matrix membrane (MMM) is a combination of polymer matrix with molecular sieve materials. Separation of gases through molecular sieving materials depends on the differences in molecular size of the gases. By combining the polymer matrix and molecular sieve materials, MMM with enhanced performance, heat, and chemical resistance can be developed.

Other types of membranes that foreseen as the promising technology to replace cryogenic separation for high purity and bulky supply of O₂ from air separation are ion transfer membranes. Ion transfer membranes are solid inorganic oxide ceramic materials with complex crystalline structures. These dense membranes allow oxygen ions to diffuse in the direction of decreasing O₂ partial pressure given an adequate electronic conductivity that allows the counter migration of electrons (Steeneveldt et al. 2006). The movement of O₂ ions down the membrane is charge compensated by the opposite movement of electrons. Then, the oxygen ions release their electrons and recombine to form molecular oxygen at the low partial pressure end. Therefore, the separation of oxygen via ion transfer membrane concept is achieved with the ability of the oxide membrane to conduct both ions and electrons (Leo et al. 2009). Oxygen-enriched air at various concentrations can be achieved in polymeric membrane, whereas ion transfer membranes can give purities of close to 100 %. However, until now both membranes have not been built for large-scale gas separations (Burdyny and Struchtrup 2010).

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Octanamine

► Alamine 336

Off-Gas from Catalytic Reforming

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The largest source of hydrogen in the refinery is the off-gas of the catalytic reforming unit. Catalytic reforming is a reaction using precious metal (platinum or rhenium)-based catalysts that converts alkane-containing naphta into two main products: aromatics and hydrogen. The produced hydrogen generally contains from 10 % to 30 % of cracked hydrocarbons ranging from C1 to C6+ as well as traces (at the ppmv level) of HCl and aromatics (Yampulski and Freeman 2010).

As a general rule the hydrogen produced in the catalytic reforming is purified via a PSA (pressure-swing adsorption) unit prior to being reintroduced in other hydrogen-consuming units of the refinery such as hydrotreatments or hydrocracking units. PSA proves to be a very profitable unit for such an application, as this technology allows to reach very high purities in hydrogen (>99 % molar) and high yield as the tail gas

flow of the adsorber, mainly composed of the hydrocarbon part of the reformer off-gas, is very small compared to the feed gas flow. Membrane-based gas permeation unit is sometimes used to purify the hydrogen contained in the off-gas of the catalytic reformer; especially it is necessary to regenerate the catalyst. In this case, when small hydrogen feed flows (up to $1000 \text{ Nm}^3 \cdot \text{h}^{-1}$) and medium hydrogen purities (between 90 % and 98 % molar) are required, gas permeation proves economically viable at the industrial scale.

Nowadays, three main membrane providers offer hydrogen purification permeators:

- *Air Products* with the *Prism*[®] silicon-coated polysulfone membranes (issued from *Monsanto*). *Air Products* claims that the life-time of the *Prism*[®] modules can be more than 15 years.
- *Ube Industries* with polyimide hollow fiber membranes.
- *Air Liquide* with the *MEDAL* polyimide and high-selectivity polyaramide membranes.

All those membranes are based on glassy polymers and offer a diffusion-based hydrogen selectivity. Today's membranes have high H_2/CH_4 selectivities (from 35 to 200 at 80 °C (Roman et al. 1991)). For instance, *Air Products* claims that a single-stage array of *Prism*[®] modules is able to raise the concentration of gases from 10 % to 30 % up to 70–90 % ([Air Products website](#)), while *Medal* membranes are able to raise the concentration of a gas at 51 bar from 86 % in hydrogen up to 98 % with a permeate pressure at 30 bar and a residue containing 52 % of hydrogen at 50 bar ([Medal Internet website](#)).

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•OH Radicals Production

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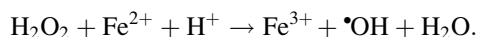
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Hydroxyl radical (•OH) is known to be a very powerful oxidizing agent for efficiently removing persistent organic pollutants (POPs) from water. It is the second strongest oxidizing agent after fluorine with a standard reduction potential of $E^\circ(\text{•OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$.

Some common techniques for generation of hydroxyl radical (•OH) can be listed as follows: (i) the chemical oxidation processes in homogeneous phase ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{O}_3$), (ii) the photocatalytic processes in homogeneous or heterogeneous phase ($\text{H}_2\text{O}_2/\text{UV}$, O_3/UV , TiO_2/UV and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$), (iii) the sonochemical processes, and (iv) the electrochemical processes (Zhou and Smith 2002).

The basic chemical oxidation process is based on the Fenton reaction, in which •OH is formed at the optimum pH of 2.8–3.0 by reaction between iron catalyst and hydrogen peroxide:



When UV_A light is applied for the photoelectro-Fenton method (PEF), there is a production of additional •OH from photoreduction reaction: $[\text{Fe}(\text{OH})]^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{•OH}$. A similar behavior is observed when sunlight is used as a photon energy source in the solar photoelectro-Fenton method (SPEF).

In the sonoelectro-Fenton (SEF) process, the additional generation of •OH is produced by water decomposition from sonolysis.

In the case of AO (anodic oxidation) and $\text{AO}/\text{H}_2\text{O}_2$, heterogeneous •OH is generated at the anode surface from water oxidation under the

application of a high current density. This process can be much more efficient when BDD (boron-doped diamond) is used as an anode instead of Pt (Brillas et al. 2009).

Through photolysis of hydrogen peroxide, hydroxyl radicals are generated by irradiating H_2O_2 under laser light at wavelength of 405 nm, and the amount of hydroxyl radical produced increases with the irradiation time (Ikai et al. 2010).

In addition, the ozonation process is also another interesting way of producing $\cdot\text{OH}$. Ozone at elevated pH (>8.5) will be decomposed into hydroxyl radicals. In the $\text{O}_3/\text{H}_2\text{O}_2$ process, often called the peroxone process, although H_2O_2 reacts very slowly with the ozone molecule in water, its conjugated base (HO^-) can rapidly react with molecular ozone to form hydroxyl radicals: $\text{HO}_2^- + \text{O}_3 \rightarrow \cdot\text{OH} + \text{O}_2^- + \text{O}_2$.

In the O_3/UV process, the reaction mechanism starts with the activation of the ozone molecule by UV irradiation to form oxygen radicals, which then recombine with water to form $\cdot\text{OH}$ radicals.

Heterogeneous photocatalytic processes such as TiO_2/UV and $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ can readily generate hydroxyl radicals on the surface of particles when absorbing UV light: $\text{h}^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$ (Zhou and Smith 2002).

As presented, technologies of hydroxyl radical ($\cdot\text{OH}$) production are diversified and are still in progress thanks to the development of new catalytic and photocatalytic nanomaterials.

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Oil-Water Emulsion

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Oil-water emulsion is a dispersion of one liquid in another one with which it is immiscible or poorly miscible. Liquids are normally an organic phase (an "oil") and an aqueous solution (a "water"), respectively. The dispersed liquid is present in the form of droplets in the continuous phase. Direct emulsions are composed of droplets of an organic liquid dispersed in an aqueous solution (O/W), while inverse emulsions are composed of aqueous droplets dispersed in an organic liquid (W/O). Emulsions play an important role in the formulation of various products such as foods; examples of O/W emulsions are dressings, artificial milks, cream liqueurs, etc., and examples of W/O emulsions are margarines and low-fat spreads. In addition, there are numerous nonfood emulsions like ore and petroleum recovery, cleaning and polishing, pharmaceutical products, cosmetics, pesticides for crop protection, bitumen (for road application), water-based paints, photographic films, paper coatings, textiles, leather, etc (Nazir et al. 2010).

Emulsions are thermodynamically unstable systems, that is to say, their free energy of formation is greater than zero, and as such will show a tendency to break (Capek 2004). Instability of emulsion occurs by creaming and coalescence. Creaming is exhibited if the two phases differ in specific gravity and if the emulsion particles are so large initially, or grow to such a size, that they are not responsive to Brownian movement. Coalescence of emulsion particles is often irreversible and is a case of true instability. Coalescence occurs when the interfacial film ruptures at the point of juncture of two particles of the discontinuous or internal phase. It may be reversible if a relatively large proportion of emulsifier is

employed and if the emulsifier has been chosen so as to afford the greatest ease of emulsification (Grayson et al. 1979). A most successful method used to choose proper emulsifying agents for a given system is HLB method. The HLB stands for hydrophile-lipophile balance. HLB number is assigned to each surface-active agent. Those materials with HLB numbers in the range of 4–6 are suitable as emulsifiers for W/O emulsion, while only those with HLB numbers in the range 8–18 are suitable for the preparation of O/W emulsion.

In the evaluation of emulsions, there are a number of fairly standardized measurements. For surface and interfacial tension, the measurements include capillary-height method, drop-weight method, ring method, etc. The viscosity of an emulsion is an important factor in determining its stability as well as from the point of view of ultimate use. Viscosity measurements may also be a guide to the type of emulsion (O/W or W/O). Three basic methods of viscosity measurement are capillary tube methods, falling ball methods, and rotational methods. It is important to determinate the type of emulsion. Unfortunately, an unequivocal determination may not always be possible, and deductive reasoning based on the data obtained from several methods may be required. Desired information may be obtained from five classic methods: dye solubility method, phase dilution method, conductivity method, fluorescence method, and wetting of filter paper. In studies of the stability of emulsions, the change in the particle-size distribution with time is often an important datum. There are, in general, four distinct methods by which this information may be obtained, i.e., by microscopic observation, by various sedimentation techniques, by light-scattering measurements, and by instrumental counting (Becher 1965).

The emulsion is prepared by mechanical disruption of the dispersed phase into the continuous phase. Conventional methods apply shear and extensional stresses to the product. Popular types of equipments are colloid mills, rotor-stator systems, high-pressure homogenizers, and ultrasonic

homogenizers, and these systems show poor control over droplet size and distribution. New methods for emulsification using microstructured systems like membrane emulsification and microchannel emulsification have received much attention. For membrane emulsification, two methods of operation are used: cross-flow membrane emulsification and premix membrane emulsification. In cross-flow membrane emulsification, the emulsion is formed by pushing the to-be-dispersed phase through a membrane into the cross-flowing continuous phase. Ideally, droplet size can be controlled primarily by the choice of the membrane, the cross-flow velocity, and the transmembrane pressure. Contrary to cross-flow emulsification, premix emulsification can be used to produce emulsions with high dispersed phase fraction, albeit that the size of the droplets is not as monodisperse as for cross-flow emulsification (Nazir et al. 2010).

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Olefin and Paraffin Separation

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Light olefins (alkenes), such as ethylene and propylene, are base chemical intermediates that are used for the production of raw chemicals and

polymers. Those olefins are separated industrially from their paraffin (alkane) counterpart in very energy-consuming distillation operations. Membrane separation could possibly constitute an attractive highly modular and less energy-consuming alternative option for olefin/paraffin separation.

Since more than 20 years, the performances of a very wide array of membrane materials for olefin/paraffin separation have been studied at lab scale mainly by academic teams. We provide here a brief overview of the advantages and limits of each membrane material family. For further reading, extensive and detailed reviews concerning the use of several types of membrane materials for olefin/paraffin separation can be found in various recent papers (Ravanchi et al. 2009; Burns and Koros 2003; Azhin et al. 2008).

Glassy Polymer Membranes

If compared to other glassy polymers offering molecular sieving properties, phenylene polyoxide offers the “best” selectivity/permeability compromise for ethylene/ethane separation (Tanaka et al. 1996; Ilcinich et al. 1992).

Concerning propylene/propane separation, 4,4'-hexafluoroisophtalenediphtalic dianhydride (6-FDA)-based aromatic polyimides favor two conditions that explain why, for comparable selectivity values, such fluorinated polyimides display higher permeabilities toward propylene than the other types of polymers (Hoehn 1974):

- Rigid polymer chains that promote molecular sieving selectivity. This can be achieved if the monomers are connected to each other via multiple chemical bonds – in order to limit free rotation of monomers – and if the polymer chains are mainly constituted of aromatic groups
- High free volume in order to favor the permeation of the fastest permeating compound

Facilitated Transport Membranes

Initially, academic research on ionic metal olefin-selective facilitated transport membranes was focused on *liquid membranes*, whether immobilized liquid membranes containing silver nitrate (Teramoto et al. 1989; Ravanchi et al. 2009) or solvent-swollen membranes (Yang and Hsiue 1996). The selectivity of this type of membrane materials is based on a reversible specific interaction of the pi electrons of olefins with certain metal ions, such as ionic silver, dissolved in the polymer matrix, which results in facilitated olefin transport of the ion-olefin coupling through the membrane. Though offering good olefin/paraffin separation performances at lab scale, those materials were subject to a loss of solvent by evaporation, which resulted in dramatic fall of olefin/paraffin separation performances.

In the latter years, new attention was paid at promising ionic silver-impregnated *solid-state polyelectrolyte membranes* based on PVP, PAZ, or PEO polymer which were not suffering from desiccation phenomena when flowing dry gases (Kim et al. 2002). Though the first results based on pure compounds were very promising, i.e., an ideal separation propylene/propane factor as high as 15,000 (Kim et al. 2002), the mixed selectivity of those types of materials was lower by orders of magnitude (Kim et al. 2003). This significant discrepancy between the ideal and the mixture could be mainly attributed to a swelling-induced plasticization of the membrane materials by short olefins and paraffins (Ko et al. 2009).

Carbon Membranes

Carbon membranes are prepared by pyrolyzing polymeric precursors. The pyrolysis aims at (1) enhancing the molecular sieving properties of the processed polymer and (2) rendering them less sensitive to plasticization. When they are carbonized at high temperatures, the polymer chains tend to transform to an inorganic structure and the transfer mechanism of sorbents inside the

membrane materials switches from a solution-diffusion mechanism to a molecular sieving mechanism.

The main limit of carbon membranes is their *brittleness*, resulting practically in a poor mechanical strength (Yoshino et al. 2003). Several authors managed to keep the pyrolyzed membrane materials flexible by incorporating pendant sulfonic acid groups in the precursor polymer and keeping the pyrolysis temperature sufficiently low in order to allow the decomposition of the sulfonic acid groups without decomposing the skeleton of the polymer matrix (Islam et al. 2005).

Zeolite Membranes

Several studies concerning the separation of propylene from propane base on faujasite (FAU zeolite) membranes (Nikolakis et al. 2001) or titanosilicate ETS (Tiscornia et al. 2008) have been published recently. The olefin/paraffin selectivity of all those materials was comparable to glassy polymers and always below 10.

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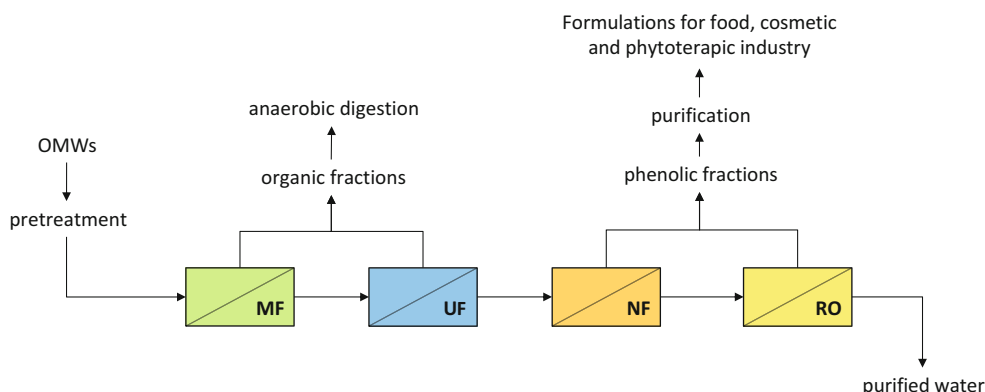
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Olive Mill Wastewater Treatment by Membrane Operations

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The extraction of olive oil generates huge quantities of wastes having a great impact on land and water environments because of their high phytotoxicity. Pressure and three-phase centrifugation systems produce a liquid effluent called olive mill wastewater (OMW).



Olive Mill Wastewater Treatment by Membrane Operations, Fig. 1 Integrated membrane process for the treatment of OMWs

Several waste management approaches, including physicochemical treatments (natural evaporation, treatment with lime and clay, oxidation), agronomic methods (land spreading), animal breeding, and biological treatments (both aerobic and anaerobic) have been proposed to reduce the polluting load and, consequently, the final waste disposal. The efficiency of the process, the complexity, and the costs involved may vary remarkably. In addition, different legislations existing in olive-oil producing countries play an important role in the selection of appropriated technologies.

Pressure-driven membrane operations, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been proposed and combined in integrated processes to obtain effluent streams from OMWs of acceptable quality for safe disposal into the environment (surface water or soil) for irrigation or even for recycling and use in the olive mill. Basically, MF and UF processes are used for primary treatment purpose, while NF and RO are used for final treatment (Cassano et al. 2013; Paraskeva et al. 2007).

Integrated systems based on the use of these processes permit to obtain a COD reduction of about 99 %, the recovery of high percentage of purified water (60–70 %) (permeate of RO membranes), a production of an organic fraction

(retentate of MF and UF membranes) which can be submitted to anaerobic digestion for the production of biogas, the recovery of a phenolic fraction (retentate of NF and RO membranes) of potential interest for food, phytoterapeutic, or cosmetic applications (Fig. 1).

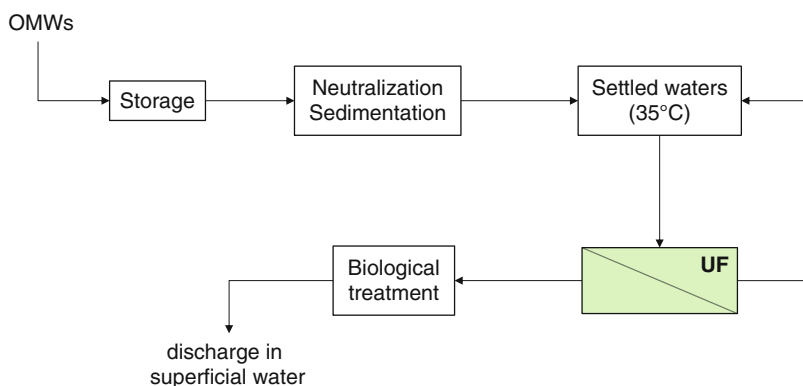
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Olive Wastewater

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Olive oil extraction processes are usually grouped into press extraction and centrifugation extraction

Olive Wastewater,**Fig. 1** Scheme of OMWs treatment with UF membranes

systems (two-phase and three-phase centrifugal olive oil extraction).

The extraction of olive oil generates huge quantities of wastes having a great impact on land and water environments because of their high phytotoxicity. Pressure and three-phase centrifugation systems produce a liquid effluent called olive mill wastewater (OMW) or vegetation water. Typically, 0.5–1.5 m³ of OMWs per 1,000 kg of olives are produced depending on the process used. OMWs appear like violet-dark brown liquids with acid reaction (pH from 3 to 6) containing great quantity of suspended matter, high degree of organic pollution (COD, 40–220 g/L; BOD, 35–110 g/L), high electrical conductivity, reducing sugars up to 60 % of the dry substance and polyphenols (0.5–24 g/L) (Takac and Karakaya 2009).

The organic content is mainly represented by polyphenols, carbohydrates, polysaccharides, sugars, nitro compounds, polyalcohols, and oil.

Ultrafiltration (UF) membranes allow to separate macromolecules and colloids having molecular weight between 500 and 250,000 Da; they can be used to remove most parts of COD from pretreated OMWs producing a permeate stream which can be submitted to a biological treatment to comply with law limits relevant to BOD and COD (Borsani and Ferrando 1996). A scheme of

OMW treatment including a concentration step via UF is depicted in Fig. 1.

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Open-Loop Cascade Diafiltration

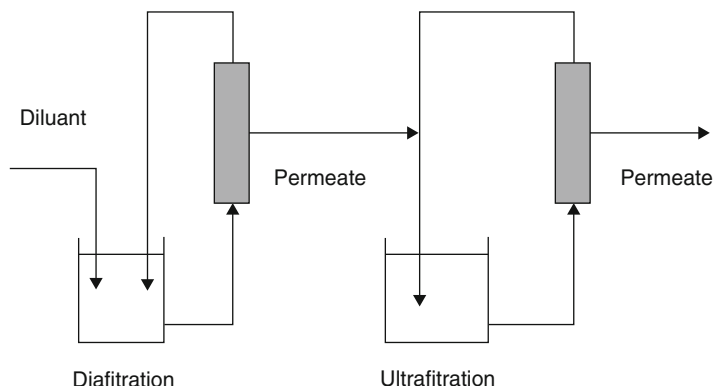
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The configuration for open-loop cascade diafiltration is shown below. The product recovery is maximized in the first stage using constant volume diafiltration and concentrated in the second stage by ultrafiltration. Ideally, the rejection coefficient of the product is zero in the first stage and 1.0 in the second stage. In the closed-loop

Open-Loop Cascade Diafiltration,

Fig. 1 Open-Loop
Cascade Diafiltration



configuration, the permeate from the second stage is used as diluant for the first stage (Fig. 1).

Optimal Process Control

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Efficient automatic control system is an essential part of every plant being operated in chemical industry. It may be implemented for various reasons: plant and environmental safety, fulfillment of varying process demands, rejection of input disturbances, optimal production desire, etc.

Process control is usually achieved via feedback policy. By measuring time-varying process outputs $\mathbf{y}(t)$ (controlled variables), such as temperature or concentration, one decides about process inputs $\mathbf{u}(t)$ (manipulated variables), such as input power to heating cell or valve position, to attain some or all of the abovementioned goals.

Classical control theory defines a fashion in which obtained measurements are used to identify values of inputs as a control law (Skogestad and Postlethwaite 2005). Its basic form can be stated as

$$\mathbf{u}(t) = f(\mathbf{y}(t))$$

$\mathbf{u}(t) = f(\mathbf{y}(t))$ where $f(\cdot)$ represents a function which can take various forms and can be designed

using analytical or numerical methods in order to establish optimal, adaptive, robust, stochastic, or any other type of process control.

Optimality of the process is measured in terms of performance criterion $J(\mathbf{y}, \mathbf{u})$. Optimal control of the process should be then set such that it minimizes this criterion. Classical problems of optimal control involve problems such as reference tracking or optimal change over control.

The most common reference tracking problem is expressed by

$$\min_{\mathbf{u}} \int_0^{\infty} (\mathbf{y} - \mathbf{y}^{ref})^T \mathbf{Q}(\mathbf{y} - \mathbf{y}^{ref}) + \mathbf{u}^T \mathbf{R} \mathbf{u} dt$$

where $\mathbf{y}^{ref}$ represents output reference (trajectory) and $\mathbf{Q}$ and $\mathbf{R}$ are so-called weighing matrices (Mikles and Fikar 2007). If this problem is considered and the controlled process is described by linear model (e.g., transfer function), function $f(\cdot)$ takes the form of a matrix-vector product, $\mathbf{K}\mathbf{y}$. Matrix $\mathbf{K}$ can be found easily using the tools of linear algebra. However, if the controlled system exhibits nonlinear behavior, more complicated techniques (e.g., dynamic optimization) are required.

Cross-References

► [Process Control in Membrane Operations](#)

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Organic Acid Production by Membrane Biotechnology with Electrodialysis (ED)

► Gluconic Acid Production in Hybrid System Membrane Bioreactor with ED

Organic Acids Recovery by Nanofiltration

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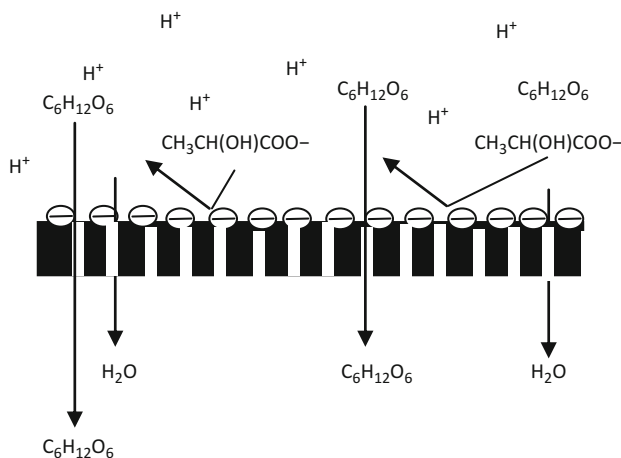
Nanofiltration (NF) is a type of pressure-driven membrane that separates solute based on the size as well as charge exclusion. A negatively charged membrane is used to repel anionic organic acid

such as lactic acid, acetic acid, citric acid, amino acid, formic acid, and oxalic acid while allowing the uncharged solutes like sugar to pass through (Fig. 1). However, if the membrane is positively charged, the adverse phenomenon will be observed. NF for organic acid recovery is always regarded as a green biorefinery method due to its low energy consumption and unique separation properties, for example, nanofiltrations can be used as a method to separate lactic acid from the nutrients, salt, and unreacted carbon in fermentation broth; thus it combines production and purification of the organic acid in a single operation unit. Commercial nanofiltration such as Osmonics (DK, DL, HL), Hydranautics (HT), Filmtec (FT), Sepro (NF2, NF3, NF20), and Koch (KO) with molecular weight cutoff of 100–350 Da are usually employed.

The retention and separation of organic acid using nanofiltration is highly dependent on solution pH, diffusivity, temperature, and pressure. The suitability of NF membrane for the separation of organic acid from fermentation broth was based on the compromise between the rejection efficiency with the targeted permeation fluxes. NF membranes are usually employed after microfiltration membranes pretreatment for cell removal. In a laboratory trial, an NF composite polyamide membrane was found to retain more than 90 % of the unconverted sugars while allowing more or less 30 % lactic acid to permeate

Organic Acids Recovery by Nanofiltration,

Fig. 1 Nanofiltration for organic acid recovery



the membrane at a flux around $110 \text{ Lm}^{-2} \text{ h}^{-1}$ at pH 5.5, temperature 37°C , and transmembrane pressure of 13 bars (Sikder et al. 2012). Recovery of lactic acid from the fermentation broth is normally achieved using the hybrid NF and electro-dialysis system whereby sodium lactate is isolated from the fermentation broth using nanofiltration and then converted to lactic acid in the electro-dialysis stage.

In organic acid recovery using nanofiltration, the efficiency of the system is measured as separation factor, $\alpha = \frac{1-R_{\text{OA}}}{1-R_{\text{IM}}}$ where R_{OA} and R_{IM} are the rejection of organic acid and impurities, respectively. In a pilot scale test using Desal-5 DK membrane, the maximum separation factor of acetic acid over arabinose was 52, when the system was operated at pH 2.9 and an applied pressure of 24.5–34.3 bar (Weng et al. 2010).

In food industry, removal of benzoic acid (preservative) from citric acid in the fruit juice was also reported. At pH 4.5, benzoic acid is uncharged and shows negative rejection (highly permeable) compared to other organic acids in the fruit juice which enable its potential recovery.

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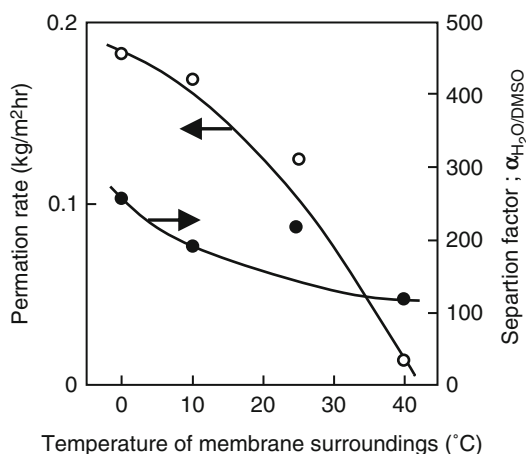
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Organic Dehydration

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Water/organic-selective membranes are effective for the dehydration of water/organic mixtures.

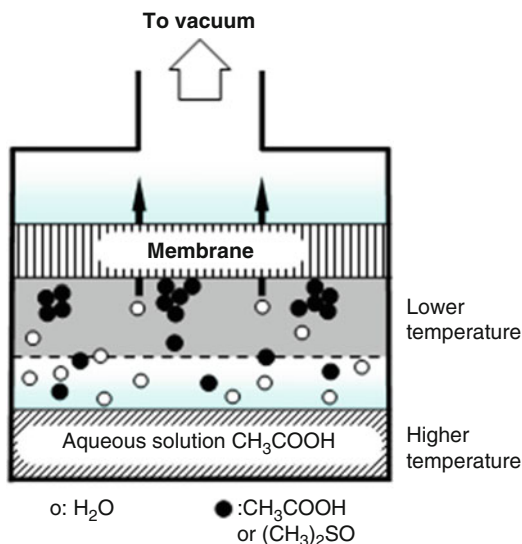


Organic Dehydration, Fig. 1 Effects of the temperature of the membrane surroundings on the characteristics of permeation and separation for an aqueous solution of 50 wt.% dimethyl sulfoxide (DMSO) through the Chito membrane in TDEV. Feed temperature: 40°C

The dehydrated organic solvents can be useful as industrial reaction solvents, washing solvents, and analytical solvents.

In Fig. 1, the permeation and separation characteristics for an aqueous dimethyl sulfoxide (DMSO) solution through a dense chitosan (Chito) membrane by TDEV (see “► [Temperature-Difference-Controlled Evaporation \(TDEV\)](#)”) are shown. In this figure, the feed was an aqueous solution of 50 wt.% dimethyl sulfoxide, the temperature of the feed solution was kept constant at 40°C , and the temperature of the membrane surroundings was lowered to less than the temperature of the feed solution (Uragami and Shinomiya 1992). Both the total permeation rate and the separation factor increased with dropping temperature of the membrane surroundings. This increase in the total permeation rate may be due to the increase in the solubility of the vapor in the membrane with decreasing temperature of the membrane surroundings, according to Henry’s law. The increase of the separation factor, i.e., the improvement of the $\text{H}_2\text{O}/\text{DMSO}$ selectivity, can be explained by the illustration shown in Fig. 2.

When the dimethyl sulfoxide and water molecules which had vaporized from the feed mixture come close to the membrane surroundings, the



Organic Dehydration, Fig. 2 Tentative separation mechanism for aqueous dimethyl sulfoxide solution through a Chito membrane in TDEV

dimethyl sulfoxide vapor aggregates much easier than the water vapor (because the freezing points of dimethyl sulfoxide and water are 18.4 °C and 0 °C, respectively) and tends to liquefy as the temperature of the surrounding membrane becomes lower. This aggregation of the dimethyl sulfoxide molecules is responsible for the increase in the H₂O/DMSO selectivity for water through the Chito membrane. The increase in the separation factor with the TDEV method, in which the temperature of the membrane surroundings is lower than the temperature of the feed solution, can be attributed to the degree of aggregation of the DMSO molecule, which is significantly governed by the temperature of the membrane surroundings. The high H₂O/DMSO selectivity of Chito membrane for an aqueous solution dimethyl sulfoxide in TDEV is significantly enhanced by both the high affinity for water of the Chito membrane and the decrease in the solubility selectivity for dimethyl sulfoxide molecules into the Chito membrane, based on their aggregation on the membrane surroundings (Uragami and Shinomiya 1992; Uragami 2008). The mechanism of permeation and separation of a dimethyl sulfoxide/water mixture through a dense Chito membrane during TDEV in Fig. 2 is effective for

understanding that of an ethanol/water mixture through a dense PDMS membrane during TDEV (Uragami 2008).

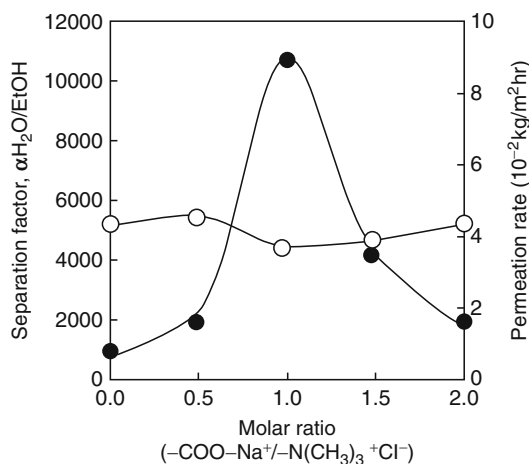
The characteristics of permeation and separation of acetic acid/water mixtures through 85/15 (v/v) PVA/malic acid (MA) membranes were investigated by EV (see “► [Evapomeation \(EV\)](#)”) and TDEV. The permeation rates increased, but separation factors for H₂O/CH₃COOH selectivity decreased with increasing permeation temperature during EV. When the temperature of feed liquid was kept constant and the temperature of the membrane surrounding was dropped, the permeation rate and separation factor for H₂O/CH₃COOH selectivity were significantly influenced by the temperature of membrane surroundings. The increase in the acetic acid concentration in the feed vapor mixture decreased the permeation rate and increased the separation factor for H₂O/CH₃COOH selectivity except 40 wt.% acetic acid content. The best separation factors were 800 in the EV and 860 in the TDEV for 90 wt.% acetic acid. The separation index of TDEV was higher than that of EV for an azeotropic mixture of acetic acid/water. TDEV in the separation of acetic acid/water mixtures through the PVA/MA membranes was more effective than EV (Isiklan and Sanli 2005).

Graft-copolymer membranes grafted 4-vinyl pyridine, acrylonitrile, and hydroxymethyl methacrylate onto poly(vinyl alcohol) and also were applied to the dehydration of acetic acid in EV and TDEV, and those membranes showed high dehydration performance (Asman and Sanli 2006; Al-Ghezawi and Sanli 2006).

Water/alcohol-selective membranes are effective for the following scenario. For example, when an aqueous solution of dilute ethanol (about 10 wt.%) produced by the bio-fermentation is concentrated by distillation, since an aqueous solution of 96.5 wt.% ethanol is an azeotropic mixture, ethanol cannot be concentrated anymore by distillation, and consequently, ethanol is concentrated by azeotropic distillation with the addition of benzene. If membranes that can preferentially permeate only water at 3.5 wt.% in an azeotropic mixture of aqueous ethanol solution can be developed, significant energy savings

would be achieved. The permeation and separation mechanisms in PV, EV, and TDEV through dense membranes consist of the dissolution of the permeants into the membrane, the diffusion of the permeants in the membrane, and the evaporation of the permeants from the membrane. Therefore, the separation of permeants in the membrane separation techniques depends on the differences in the solubility and diffusivity of the permeants in the feed mixture. When the structure of water/alcohol- and water/organic liquid-selective membranes is dominically designed, hydrophilic materials can be recommended as membrane materials. Therefore, an increase in the solubility of water molecules into the membrane during the solution process can be expected. In order to raise the affinity of membranes for water molecules, membranes with dissociation groups introduced into their structure are used for dehydration from organic solvents.

The dehydration of an ethanol/water azeotrope during EV using polyion complex cross-linked chitosan composite (q-Chito-PEO acid PIC/PES composite) membranes, constructed from quaternized chitosan (q-Chito) and polyethylene oxydiglycolic acid (PEO acid) on a porous polyethersulfone (PES) support, was investigated (Uragami and Yamada 1999, 2003). Both the q-Chito/PES composite and the q-Chito-PEO acid polyion complex/PES composite membranes showed high H₂O/EtOH selectivity for an ethanol/water azeotrope. Both the permeation rate and the H₂O/EtOH selectivity were enhanced by increasing the degree of quaternization of the chitosan molecule, because the affinity of the q-Chito/PES composite membranes for water was increased by introducing a quaternized ammonium group into the chitosan molecule. Q-Chito-PEO acid PIC/PES composite membranes prepared from an equimolar ratio of carboxylate groups in the PEO acid versus quaternized ammonium groups in the q-Chito showed the best separation factor for H₂O/EtOH selectivity without lowering the permeation rate, as shown in Fig. 3. With an increasing molecular weight of PEO acid, the separation factor for H₂O/EtOH selectivity increased, but the permeation rate almost did not change. The separation factor



Organic Dehydration, Fig. 3 Permeation and separation characteristics for an azeotropic mixture of ethanol/water through q-Chito/PEO acid 4000 polyion complex/PES composite membranes during EV as a function of the molar ratio between the carboxylate groups in PEO acid 4000 and the ammonium groups in q-Chito at 40 °C

for aqueous solutions of 1- and 2-propanol was also maximized at an equimolar ratio of carboxylate groups and ammonium groups and was greater than for an ethanol/water azeotrope.

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Organic Solvent Nanofiltration (OSN)

► Solvent-Resistant Nanofiltration

Organic Vapor Recovery

► VOC Recovery

Organotypic Membrane Systems

► Bioartificial Organs, Membrane Operations of

Oriented Immobilized Anti-hIgG via Fc Fragment-Imprinted Cryogels

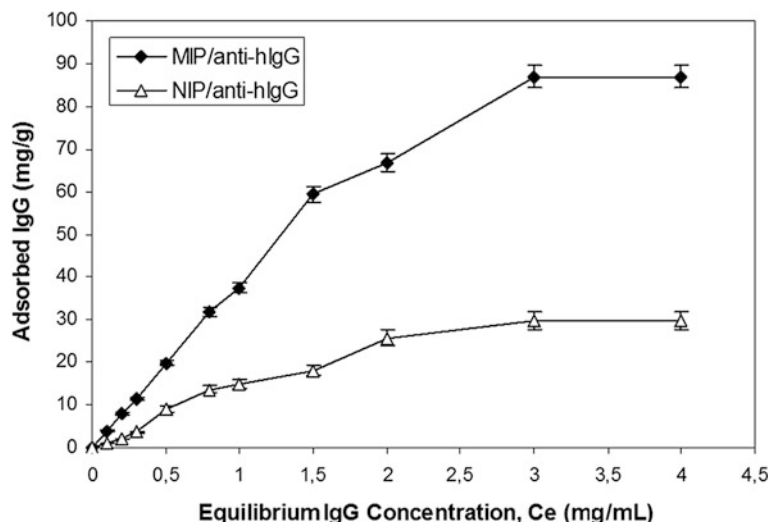
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Antibodies exhibit unique binding properties, high affinity and specificity towards a wide range of natural and synthetic targets. Because of these properties, antibodies are utilized in many applications including therapeutics, diagnostics, research in biology and biotechnology, immunoaffinity chromatography, etc. (Huse et al. 2002). For medical applications, immunoglobulins (IgGs) have been purified using a combination of various methods like precipitation and chromatographic techniques including hydrophobic interaction, histidine affinity, ion exchange, dye affinity, and metal-chelate affinity

(Tishchenko et al. 2002; Yavuz and Denizli 2005; Denizli 2011). Antibody immobilization is an important step in the preparation of chromatographic immunoaffinity column. The recognition part of the antibody has to be accessible to maintain the antibody's functionality and to detect the analyte molecule. Therefore, during immobilization, the proper orientation of antibodies on the surface of the solid support is crucial (Batalla et al. 2008). There are some more specific techniques using immobilized protein A or G for the immobilization of antibodies by the F_c region. These are more efficient techniques resulting to the oriented immobilization of antibodies and thus giving rise to highly accessible antigen-binding sites on the antibody and increase in the activity of the immobilized antibody molecule (Hober et al. 2007). However, despite their general use as effective ligands for the oriented immobilization of antibodies, they have some drawbacks in their economical value, reusability, and concerns over the clearance of leached ligand (Low et al. 2007). Small antibody fragments can be evaluated as simple, inexpensive, more stable, general purpose ligands to be an alternative to protein A or G. In combination with an oriented immobilization method, these small antibody fragments allow an increased degree of immobilization of well-oriented and active antibodies per solid support surface area, hence facilitating higher antibody-antigen complex formation (Bonroy et al. 2006). Fc fragment-imprinted poly(hydroxyethyl methacrylate) cryogel (MIP) can be used for the oriented immobilization of anti-hIgG for IgG purification from human plasma. Non-imprinted poly(hydroxyethyl methacrylate) cryogel (NIP) can be also used for random immobilization of anti-hIgG to compare the adsorption capacities of oriented (MIP/anti-hIgG) and random (NIP/anti-hIgG) cryogel columns. IgG adsorption capacity is found to be three times higher than the NIP/anti-hIgG column (29.7 mg/g) for the MIP/anti-hIgG column (86.9 mg/g) (Fig. 1). Higher IgG adsorption capacity was observed from human plasma (up to 106.4 mg/g) with the MIP/anti-hIgG cryogel column. The results obtained are promising and show that F_c fragments of antibodies with

Oriented Immobilized Anti-hIgG via Fc Fragment-Imprinted Cryogels, Fig. 1

IgG adsorption amounts of MIP/anti-hIgG (oriented) and NIP/anti-hIgG (random) cryogel (Bereili et al. 2013)



an oriented immobilization method can be considered as a potential candidate for IgG purification human plasma (Bereili et al. 2013).

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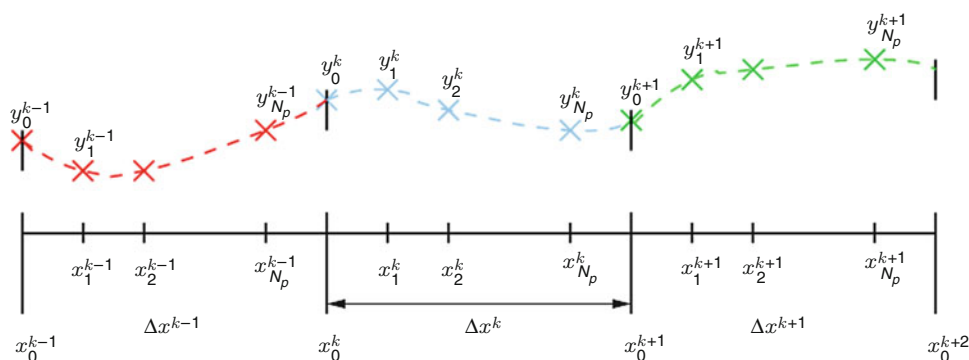
Orthogonal Collocation Method

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This method represents an approximation technique which is successfully used to solve multipoint boundary value problems. Such problems arise in engineering applications frequently when it is desired to simulate processes described by partial differential equations (Kaldis et al. 2000; Sousa and Mendes 2004), to model complex processes (Ganguly and Bhattacharya (1994); Sousa et al. 2002) or to compute optimal process control (Fikar et al. 2010).

The principle is to approximate the behavior of any nonlinear function $f(\mathbf{x})$ by the sum of basis functions (most preferably polynomials) on some chosen number of intervals. Approximation function on the k th interval, Y^k , can be written as



Orthogonal Collocation Method, Fig. 1 Schematic representation of orthogonal collocation method

$$\mathbf{Y}^k(\mathbf{y}^k, x) = \sum_{i=0}^{N_p} y_i^k \phi_i^k(x)$$

where $\mathbf{y}^k$ is a vector of N_p+1 collocation points which represent weighting factors (coefficients) for vector of functions ϕ^k . If polynomial approximation is considered, function ϕ_i^k is an N_p th order polynomial. To guarantee the orthogonality of resulting approximation and to achieve other useful properties, orthogonal polynomials (such as Chebyshev, Lagrange, and other types) are used. For the case of Lagrange polynomials, function ϕ_i^k can be written as follows:

$$\phi_i^k(x) = \prod_{j=0, j \neq i}^{N_p} \frac{x - x_j^k}{x_i^k - x_j^k}.$$

This is illustrated in Fig. 1 which shows three consecutive intervals of approximation.

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Overall Permeation Reduction Coefficient

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Overall permeation reduction coefficient. In *membrane technology*, the so-called overall permeation reduction coefficient (*PRC*) refers to a coefficient indicating quantitatively the overall reduction of permeability (or, equivalently, reduction of permeance or flux) of a species because of the concurrent actions of different phenomena, like, as the most common instances,

concentration polarization and *inhibition*. The most general definition of PRC can be provided as follows:

$$[\text{Flux}]_i^{\text{Actual}} = (1 - PRC_i) \times [\text{Flux}]_i^{\text{Max}} \quad (1)$$

Equation 1 simply states that the actual flux (i.e., in the presence of phenomena reducing membrane performance) is equal to the product of the maximum flux (i.e., free of unwanted phenomena) by a certain reduction factor. According to this definition, PRC_i approaches the unity value (flux tending to zero) when the unwanted phenomena control permeation, whereas it approaches zero when those phenomena are negligible.

If considering that the overall permeation reduction is due to the coupled effect of *concentration polarization* and *inhibition*, then, under the validity of Henry's law hypotheses for the inhibiting species, PRC_i can be expressed as a function of both CPC_i and IC_i as (Caravella et al. 2010):

$$PRC_i = 1 - (1 - CPC_i)(1 - IC_i) \quad (2)$$

where CPC_i and IC_i are the *concentration polarization coefficient* and the *inhibition coefficient*, respectively.

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Oxidative Coupling in Membrane Reactors

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Oxidative coupling of methane according to
 $2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$ is a promising

way to transform natural gas into ethylene and ethane. From numerous classical co-feed experiments in packed bed reactors it follows that for a high C_2 selectivity of about 70 %, the CH_4/O_2 ratio must be high. To ensure a high C_2 selectivity, the reaction has to be performed at low oxygen partial pressure. This situation can be ensured by applying the concept of distributed oxygen dosing in “membrane distributor reactor” with dense (perovskite-like ceramic, silver) or porous membranes. The accepted reaction mechanism assumes as first step the formation of CH_3 radicals on a heterogeneous catalyst. After this heterogeneous step, the combination of two CH_3 radicals to ethane is proposed in a homogeneous gas phase reaction, followed by an oxidodehydrogenation of the ethane to ethylene. This reaction chain can be realized in a catalytic membrane reactor with oxygen supply from surrounding air applying established heterogeneous catalysts like 2 wt% Mn/5 wt% Na_2WO_4 on SiO_2 for the CH_3 formation (Kondratenko and Baerns 2008). By supplying the oxygen through the reactor wall, a rather low and constant oxygen partial pressure in axial direction of a tubular reactor can be achieved which should be beneficial for selectivity. Hot spots and explosive mixtures – like often observed for co-feed reactors – can be avoided in the case of the membrane distributor reactor (Dittmeyer and Caro 2008; Caro 2010). However, whereas best C_2 yields in classical packed bed reactors with an oxygen/methane co-feed reach 30 %, best membrane reactor data are of the order of 15 % (Tan and Li 2006) or 17 % (Czuprat et al. 2010).

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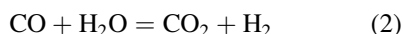
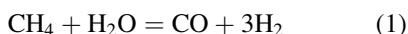
Oxidative Steam Reforming

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Autothermal reforming or oxidative steam reforming is a combination of conventional steam reforming of the fuel (endothermic reaction) with the partial oxidation of a small amount of the fuel (exothermic reaction) in order to achieve an autothermal reaction that proceeds without external input of energy.

The most studied autothermal reforming is the conversion of methane to hydrogen. The overall chemical reactions taking place in the autothermal reforming of methane include steam reforming (Eq. 1), water-gas shift (Eq. 2), and total oxidation (Eq. 3). The energy generated by the oxidation reaction and WGS is used for the SMR:



This reaction system can be carried out efficiently in a membrane reactor as the extraction of hydrogen during the reaction shifts the equilibrium reactions toward completion at moderate temperatures, and thus the extent of oxidation reaction to achieve autothermal reforming is moderate.

One of the problems of autothermal reforming carried out in membrane reactors is the mismatch between the oxidation reaction rate and the reforming reaction rate. The oxidation is often much faster than the reforming, and for this reason, in packed bed membrane reactors, a high temperature region is obtained at the beginning of the bed followed by a low temperature region at the end of the bed. This could cause problems to the membranes that could be damaged by high temperatures while does not work properly (low

flux – see Richardson equation) at lower temperatures.

To circumvent these problems, fluidized bed membrane reactors are often proposed for this kind of reaction system, as the solid circulation inside the reactor allows a virtually isothermal condition even in case of highly exothermic reactions.

Examples of autothermal reforming (ATR) (or oxidative steam reforming) reactions also include the ATR of ethanol and methanol or the ATR of naphtha. All these reactions have been successfully tested in membrane reactors for pure hydrogen production.

Oxyfuel

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Synonyms

[Oxyfuel combustion](#)

The name is derived from the process: a mixture of oxygen and a gaseous, liquid, or solid fuel is burnt in a nitrogen-free atmosphere which consists of oxygen and an easy to separate second gas, usually carbon dioxide. If fuels like natural gas, oil, or coal are combusted with pure oxygen instead of air as oxidant, nitrogen as an inert component is not heated. Therefore, the burning unit can be smaller, the flame temperatures are higher, and the fuel consumption is reduced. Depending on the fuel, the flue gas consists of CO_2 and H_2O only. After condensation of H_2O , the flue gas consists of only CO_2 which can be sequestered or used in chemical processes. But not only the mass and volume of the flue gas become smaller, due to the absence of nitrogen, also no NO_x is formed.

The oxyfuel combustion process is one of several possible technologies to separate and

sequester CO_2 from fossil fuel burning especially in electric power stations. However, electricity generation by the oxyfuel process is more expensive than in a traditional air-fired plant. The main cost factor of the oxyfuel process is the production of almost pure oxygen. Perovskite-type mixed conducting ceramics can theoretically separate oxygen with 100 % purity from air. Some of the CO_2 is in a loop used for sweeping the oxygen from the membrane separator to the combustion chamber thus reducing the oxygen partial pressure on the permeate side of the membrane to have a constant high driving force for oxygen permeation. This sweeping technique with some of the CO_2 in a loop requires CO_2 -stable oxygen-conducting membranes. Since most of the mixed conducting perovskite-type ceramics contain alkaline earth metal cations, these materials are not suitable since they form carbonates (for thermodynamic reasons also at high temperatures because of the high CO_2 partial pressure). Therefore, new CO_2 -stable mixed conducting or dual-phase materials have to be developed.

Since the fuel is combusted in an O_2/CO_2 atm, this combustion with diluted oxygen reduces the flame temperature which reduces the costs for special high temperature-resistant materials. The amount of the second inert gas can control the flame temperature of the combustion: Without any dilution gas, the combustion temperature can become too high. On the other hand, if the CO_2 concentration is much less than 80 % (nitrogen content of air), higher flame temperatures can be reached which is desired.

However, the few pilot plants evaluating the feasibility of the oxyfuel concept use oxygen production by cryogenic air separation after Linde (Callide Oxyfuel Project; Callide Oxyfuel Pilot Project; CCS Vattenfall Pilot Oxyfuel Project). In 2006 in the Schwarze Pumpe industrial area in East Germany, construction work started on the world's first "carbon-dioxide free" power station testing the oxyfuel concept on a pilot scale. However, the owner Vattenfall stopped carbon capture R&D at the plant in 2014 because "its costs and the energy it requires makes the technology unviable" ([http://www.thelocal.se/20140507/vattenfall-abandons-research-on-co2-](http://www.thelocal.se/20140507/vattenfall-abandons-research-on-co2-storage)

[storage](#)). In the Callide oxyfuel project, carbon dioxide capture started in Dec. 2012. In March 2015, the Callide Oxyfuel Project demonstration phase comes to a close after 2 years and 9 months successfully proving 10,000 h of oxyfuel combustion, and 5,500 h of carbon dioxide plant operation. Since the usual oxygen purity of 99.5 % as obtained in the Linde technique is not necessary for oxyfuel, the Linde technology can produce oxygen with 95 % purity in a cost-effective way which is competing with the ceramic membrane technology. Organic polymer membrane permeation is not competitive since it cannot produce the necessary oxygen purity of ≥ 95 % purity in a single step.

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Oxyfuel Combustion

► Oxyfuel

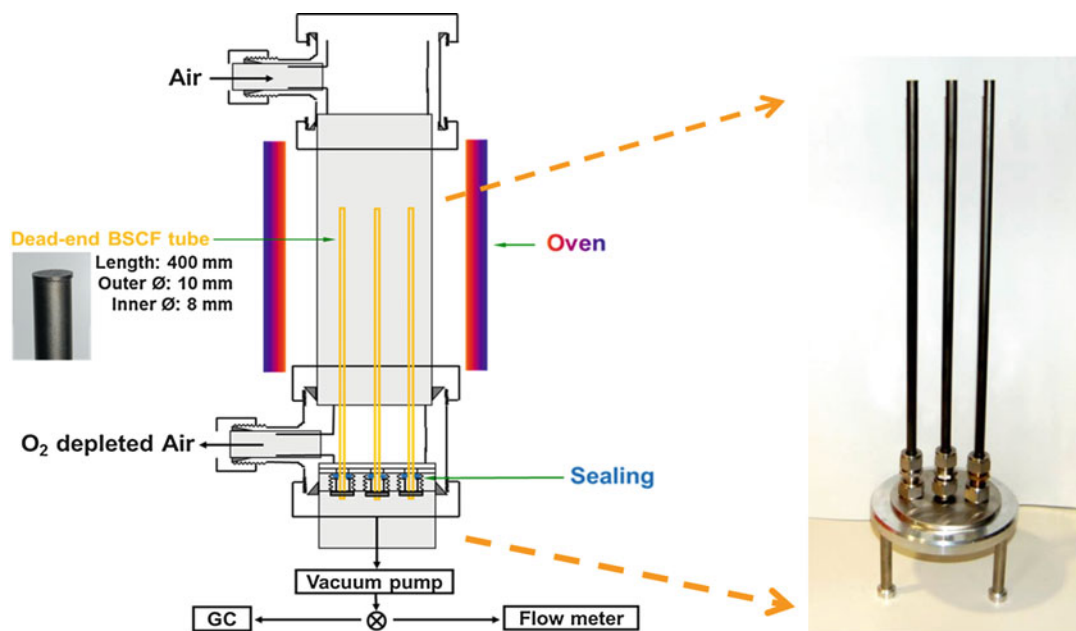
Oxygen Separation

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Synonyms

Air separation

Oxygen can be separated from air by different separation techniques such as cryogenic air distillation after Linde, pressure swing adsorption using coals for kinetic separation (the slightly



Oxygen Separation, Fig. 1 Photo and scheme of the three-tube oxygen production demonstration unit at Leibniz University of Hannover (copyright Caro, Univ. Hannover). Oxygen from surrounding air enters the BCFZ material on the shell side, diffuses via vacancies in the

oxygen lattice to the core side of the one-end-sealed BSCF tubes where it is released into the gas phase. To have a high-oxygen partial pressure difference over the membrane, the permeated oxygen is removed by vacuum pumping

smaller oxygen diffuses faster than nitrogen into the pores of the coal), or Li-exchanged zeolites like Li-LTA/Li-FAU for thermodynamically controlled separation (the more polar nitrogen is strongly adsorbed by the zeolite than the less polar oxygen). Also organic polymer hollow fiber membranes are used for oxygen/nitrogen separation, but they produce in general lower gas purity. The amount and purity of the oxygen to be produced decides about the economy of the separation techniques to be applied.

Perovskite membranes allow principally a new route for oxygen separation from air, however, at elevated temperatures of 750 °C to 900 °C. The high temperatures are necessary for a high-oxygen ion mobility and to avoid membrane damage (if CO₂ is present in low concentrations, carbonates do not form at high temperatures, see Ellingham diagram). As long as there is a sufficient gradient of the oxygen partial pressure (better: activity) over the membrane, oxygen will enter the perovskite material on the high-oxygen partial pressure side (feed side) and leave the

membrane on the low-oxygen partial pressure side (permeate side). The low-oxygen partial pressure can be achieved by continuous vacuum pumping as the most effective and economic technique but also with sweep gases. In the latter case, the sweep gases and oxygen must be separated again (if steam is used, the membrane can be damaged at the high permeation temperature). Another option to reduce the oxygen partial pressure on the permeate side is the consumption of the permeated oxygen in a catalytic partial oxidation (e.g., by consuming oxygen in a methane partial oxidation to synthesis gas).

Figure 1 shows a three-tube perovskite membrane module with 1 cm (outer diameter) Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) tubes purchased from Fraunhofer IKTS (Fraunhofer Institute for Ceramic Technologies and Systems, Dresden-Hermsdorf, Germany). The permeator has been erected during November 2012–April 2013 at Leibniz University of Hannover copying a prototype oxygen separation permeator developed by Dr. R. Kriegel (Fraunhofer IKTS, Hermsdorf)

(Kriegel et al. 2010; Schulz et al. 2011). The permeator is gastight up to an operation temperature of 950 °C, membrane area 400 cm², and dead-end BSCF tubes.

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Oxygen Transport Ceramic Membranes: Perovskite and Nonperovskite

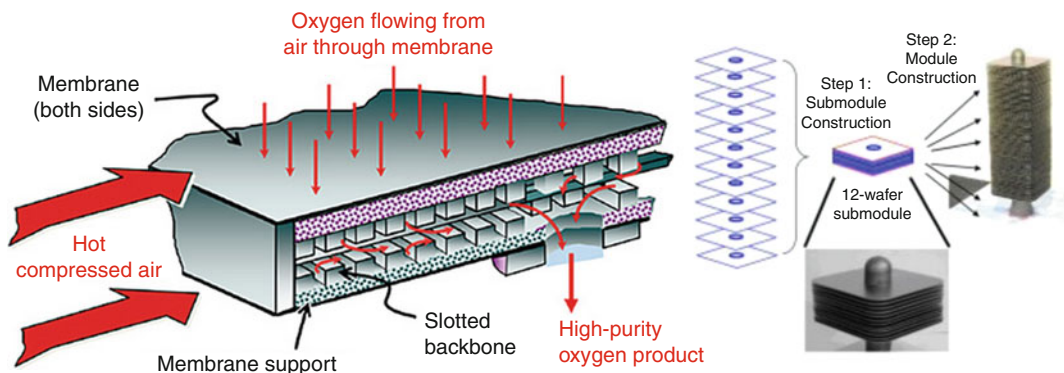
Vesna Middelkoop
Flemish Institute for Technological
Research – VITO, Mol, Belgium

Current State of Oxygen Transport Ceramic Membranes Development

For more than a decade, there has been considerable interest in dense inorganic (ceramic) oxygen separation membranes as they offer a potentially

attractive means of producing high-purity oxygen from air for use in the next generation of industrial processes and clean energy applications. Such applications are centered around oxy-combustion, coal gasification (membranes are integrated as power plant components, see example in Fig. 1), or commercial chemical reactions for conversion of natural gas and production of syngas and hydrocarbons (membranes are integrated as catalytic membrane reactors) in addition to the development of electrochemical devices (solid oxide fuel cells, SOFC) utilizing thin dense membranes of oxygen ion conductor (Dong and Jin 2012; Dong et al. 2011; Hashim et al. 2011; Thursfield and Metcalfe 2004; Skinner and Kilner 2003).

This class of membranes is often referred to in the literature as oxygen transport membranes (OTM) or ion transport membranes (ITM). Currently at the forefront of the development and deployment of oxygen producing membrane-based systems are a couple of large-scale funded programs worldwide such as the EC Seventh Framework Programs CARENA, DEMCAMER and HETMOC, and OXYCOAL-AC and MEM-BRAIN (Germany); US DOE's Vision 21 R&D Program; the Australian COAL21; the Japanese NEDO programs; and the "863" and "973" programs (national research and development programs in China) (<http://www.netl.doe.gov/technologies/coalpower/ewr/co2/oxy->



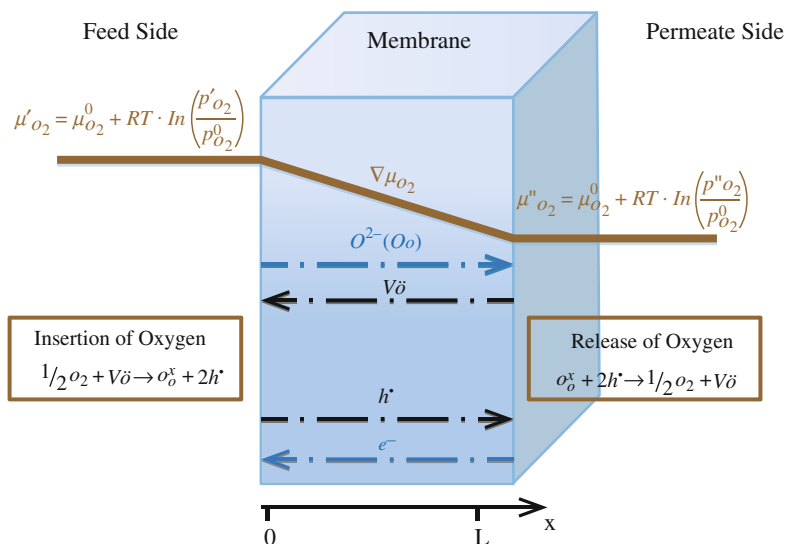
Oxygen Transport Ceramic Membranes: Perovskite and Nonperovskite, Fig. 1 Example of the design and construction of planar membranes (Air Products' ITM oxygen technology) providing high oxygen fluxes and

assembled into "multi-wafer" commercial-scale modules for a 5 TPD subscale engineering prototype (SEP) pilot plant (Reproduced with permission from DOE/NETL (2010))

Oxygen Transport Ceramic Membranes:

Perovskite and Nonperovskite,

Fig. 2 Schematic illustration of oxygen ion transport through MIEC membrane by the vacancy-hopping mechanism (Reproduced from Wei et al. (2013) with permission from Elsevier)



combustion/otm-based.html; <http://www.netl.doe.gov/technologies/coalpower/gasification/projects/gas-sep/40343.html>; Kneer et al. 2010).

Oxygen Transport Mechanism

These emerging approaches to oxygen separation rely on exploiting the unique properties of the materials that are fabricated into membranes. When they are thermally activated to sufficiently high temperatures (typically from 700 °C to 950 °C) and exposed to an oxygen partial pressure gradient, oxygen anions and electrons continuously migrate through the crystal lattice counter-currently with electrons (see Fig. 2).

Perovskite- and Non-perovskite-Based Membranes

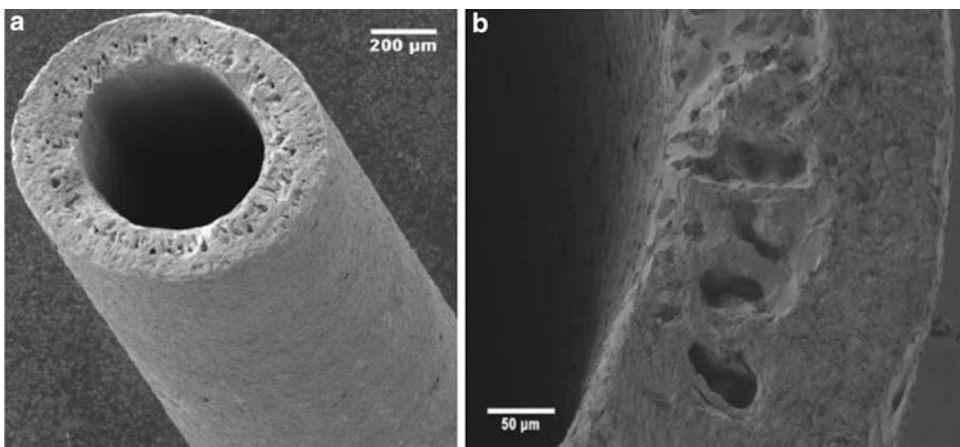
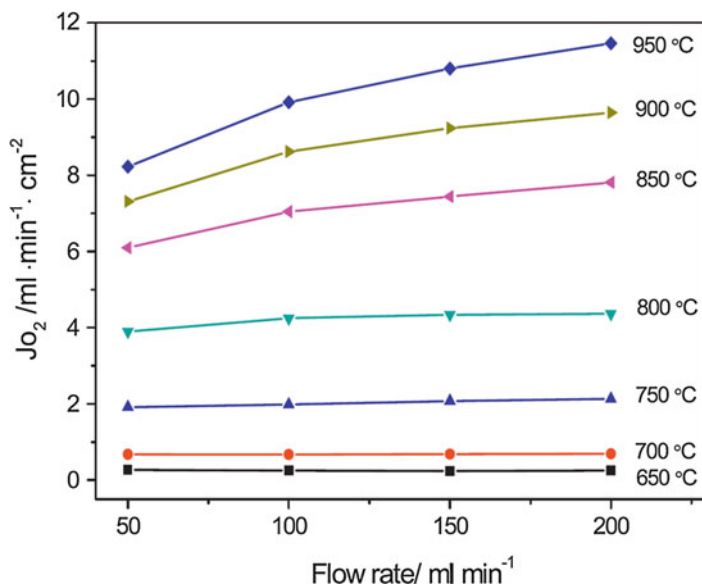
A wide variety of mixed ionic-electronic conducting (MIEC) oxides for high-temperature membrane separation have been investigated alongside novel chemical doping, synthesis, and processing routes. All MIEC conductors that are being considered for this purpose fall into two main groups: perovskite-based oxides (both of the perovskite $\text{ABO}_{3-\delta}$ structure and perovskite-related oxides of the $\text{A}_2\text{BO}_{4+\delta}$ structure) and

fluorite-based oxides (i.e., non-perovskites of the $\text{A}_{\delta}\text{B}_{1-\delta}\text{O}_{2-\delta}$ and $\text{A}_{2-\delta}\text{B}_{2-\delta}\text{O}_3$ structures). Furthermore, dual-phases composite membranes (e.g., $\text{Ce}_{0.8}\text{Gd}_{0.15}\text{Cu}_{0.05}\text{O}_{2-\delta}$ - $\text{SrFeO}_{3-\delta}$, CGCO-SFO) can be considered as another possibility for oxygen separation by combining a perovskite oxide phase (as an oxygen ionic and electronic conductor) and fluorite oxide phase (as an oxygen ionic conductor) in order to accommodate the performance and durability requirements of the membrane (Sunarso et al. 2008; Fang et al. 2015).

One of the primary industrial requirements for efficient membrane-based processes is a sufficiently high transmembrane oxygen flux which is inversely proportional to membrane thickness. Moreover, taking into consideration a higher surface area to volume ratio, hollow fiber geometry is favored over planar or tubular membranes. When the oxygen permeation data with accompanying chemical and mechanical stability at elevated temperatures and under different atmospheres are compared, to date, the most promising and readily available among the oxygen transport membranes belong to the $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{1-x}\text{Fe}_y\text{O}_{3-\delta}$ and $\text{La}_x\text{Sr}_{1-x}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ perovskite families, namely, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582), $\text{BaZr}_x\text{Co}_y\text{Fe}_z\text{O}_{3-\delta}$ (BCFZ) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428). The highest reported oxygen permeation fluxes are those of 0.3 mm thick BSCF5582 hollow fibers,

Oxygen Transport Ceramic Membranes: Perovskite and Nonperovskite,

Fig. 3 Highest reported oxygen flux values of BSCF5582 hollow fiber membrane as a function of temperature and sweep gas rate (Reproduced from Han et al. (2013) with permission from Elsevier)

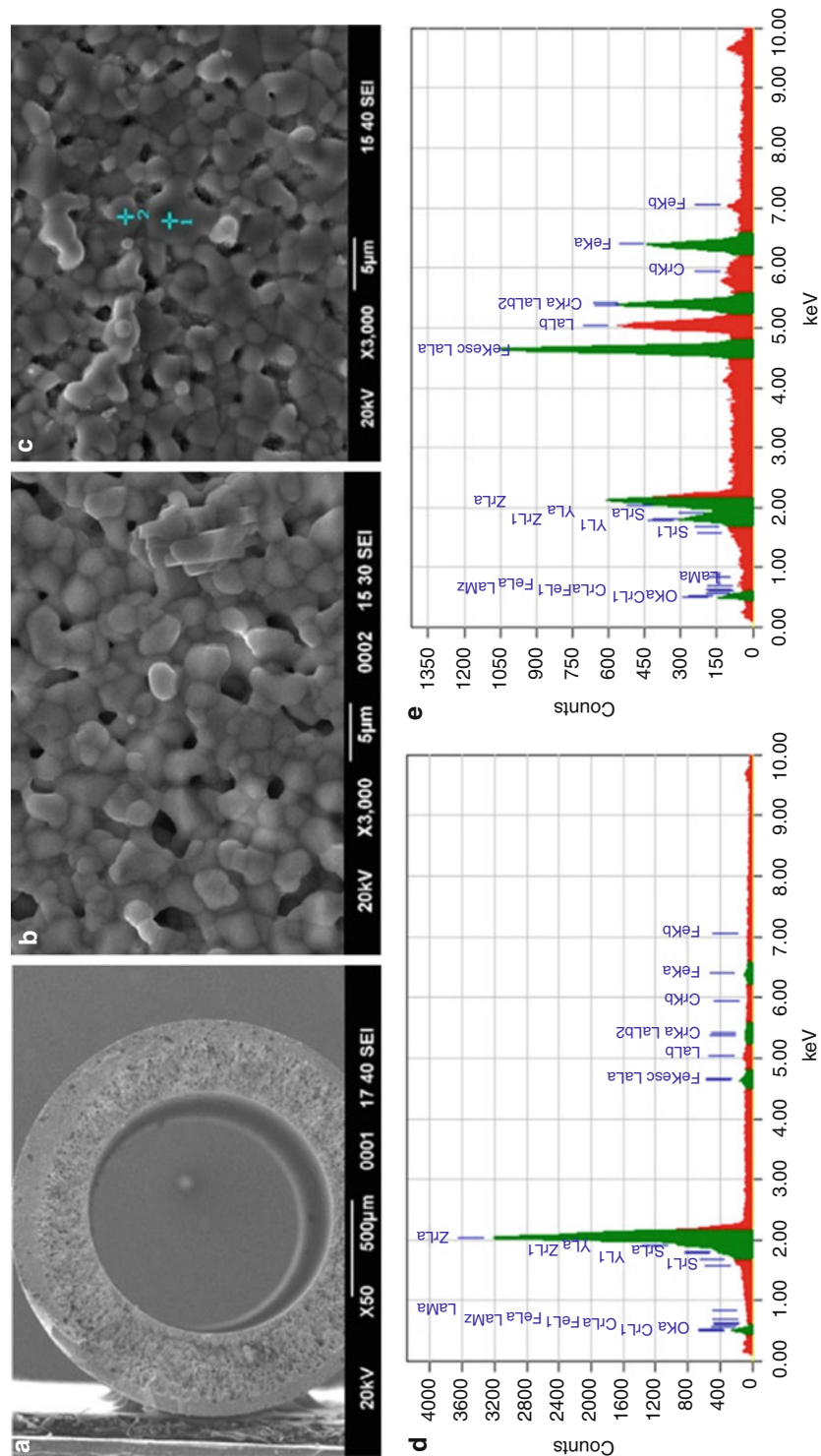


Oxygen Transport Ceramic Membranes: Perovskite and Nonperovskite, Fig. 4 SEM cross section of a dense BCFZ perovskite hollow fiber with an outer diameter of 0.88 mm, wall thickness of 0.175 mm, 11.9 cm long, and a high mechanical stability of 175 ± 15 MPa. Oxygen

permeation flux through this BCFZ hollow fiber membrane was 7.6 ml/min/cm^2 at 900°C at a flow rate of 150 ml/min of air supplied to the shell side and a helium sweep of 30 ml/supplied to the core side of the fiber (Reproduced from Schiestel et al. (2005) with permission from Elsevier)

$11.46 \text{ mL min}^{-1} \text{ cm}^{-2}$ at 950°C and a helium sweep of 200 ml min^{-1} (see Fig. 3). The BCFZ hollow fibers (shown in Fig. 4) have slightly lower oxygen fluxes but offer greater long-term stability. LSCF6428 exhibits desirable chemical stability and mechanical strength but much lower fluxes than BSCF5582 and BCFZ (up to $1 \text{ mL min}^{-1} \text{ cm}^{-2}$) (Han et al. 2013; Schiestel

et al. 2005; Wang et al. 2009). However, it is worth noting that the chemical stability of Co-rich perovskites containing alkaline earth metals (typically BSCF5582) is affected in the presence of CO_2 (they tend to form carbonates) causing a decrease in flux (Arnold et al. 2007; Xu et al. 2012). On the other hand, some of the perovskite-related materials (such as



Oxygen Transport Ceramic Membranes: Perovskite and Nonperovskite, membrane ($J(O_2) \sim 0.16 \text{ mL min}^{-1} \text{ cm}^{-2}$): (a) cross section, (b) core side surface, (c) shell side surface, (d) and (e) are chemical compositions for spots 1 and 2, respectively. (Reproduced from Liu et al. (2012) with permission from Elsevier)

$\text{CaTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{La}_2\text{NiO}_{4+\delta}$ with fluxes up to $0.45 \text{ mL min}^{-1} \text{ cm}^{-2}$) (Klande et al. 2011) as well as non-perovskite types (e.g. $\text{Sr}_4\text{Fe}_4\text{Co}_4\text{O}_{13+\delta}$ with fluxes up to $0.30 \text{ mL min}^{-1} \text{ cm}^{-2}$) (Balachandran et al. 1995) and dual phase composite membranes provide relatively low fluxes (e.g., $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}-\text{Gd}_{0.2}\text{Sr}_{0.8}\text{FeO}_{3-\delta}$, $\text{Ce}_{0.8}\text{Gd}_{0.15}\text{Cu}_{0.05}\text{O}_{2-\delta}-\text{SrFeO}_{3-\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}+\text{SrCO}_3+\text{Co}_3\text{O}_4$: 0.80, 0.84 and $93 \text{ mL min}^{-1} \text{ cm}^{-2}$ respectively) but they are found to have much greater structural and chemical stability in a reducing atmosphere (Zhu et al. 2008; Fang et al. 2015; Zhang et al. 2015).

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Oxygen-Enriched Air (OEA) Production by Membrane Reactors

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Air with increased oxygen content has different applications ranging from sub-aqua diving and medical treatments to processes like waste burning, FCC catalyst regeneration, preparation of synthesis gas for ammonia production, Claus plants, and high-temperature furnaces and kilns.

The reduction of the inert nitrogen as a ballast is of advantage in several processes. When increasing the oxygen content of air from 21 % to 30 %, there is 40 % less nitrogen per oxygen unit, and membranes of modest selectivity (3–5) and higher oxygen flux are preferred.

OEA can be produced by mixing air with pure oxygen from cryogenic air distillation after Linde or by pressure swing adsorption. Membranes can produce OEA in two different ways:

- (i) There exists a variety of commercial organic polymer membranes with a preferential oxygen transport. Since oxygen has a slightly smaller molecule size and it undergoes less interaction than the quadrupolar nitrogen, oxygen (plus carbon dioxide + water vapor) permeates faster through the polymer film than nitrogen and argon. This can be used to produce nitrogen as retentate on the high-pressure side and an oxygen-enriched air on the low pressure permeate side. If the target product is nitrogen on the high-pressure feed side, the oxygen-enriched permeate is called “waste gas.” It is estimated that for an oxygen purity of 30 % and a capacity $< 15,000 \text{ Nm}^3/\text{h}$, the investment, operating, and maintaining costs are two thirds to three fourths of cryogenic and PSA technology. Often, the spiral wound geometry is preferred and the pressure difference across the membrane is maintained

by a vacuum pump on the permeate or a compressor/van on the feed side (Puri 2011).

- (ii) Recently, perovskite-type high-temperature ceramic membranes have been proposed for OEA production (Liang and Caro 2011). Here the fee is slightly pressurized air of about 2 bar (O_2 partial pressure ≈ 0.4 bar). As sweep gas, air of typically 1 bar (O_2 partial pressure ≈ 0.2 bar) is applied. Because of the difference in oxygen partial pressure, there is an oxygen transport from the feed to the permeate side until the O_2 partial pressure on the permeate side also reaches 0.4 bar, which is air with 40 % O_2 at 1 bar (Wang et al. 2005; Hamel et al. 2006).

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Packed Bed Membrane Reactor

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The fixed bed (or packed bed) membrane reactor configuration is the first and most studied configuration for membrane reactors. This is because the first studies on membrane reactors focused on the effect of the gas permeation through membranes on the reaction system (which is often a conventional packed bed reactor).

In a packed bed membrane reactor, the catalyst is confined in fixed bed configuration, and it is in contact with a permselective membrane. The most used packed bed configuration is the tubular one where the catalyst may be packed either in the membrane tube or in the shell side, while the permeation stream is collected in the other side of the membrane (in case of hydrogen-selective membranes) or one reactant is feed on the other side of the membrane (in case of oxygen-selective membrane).

For multi-tubular membrane reactor configurations, the catalyst in tube configuration can be preferred especially for construction reason and for the extent of bed-to-wall mass and heat transfer limitations which can be very detrimental in the catalyst in shell configuration.

Often, a sweep gas can be used in the permeation side of the membrane in order to keep the permeation hydrogen partial pressure as low as possible for minimizing the membrane area required for the hydrogen separation. This practice is, for example, very useful if hydrogen for ammonia plant is being produced, in which case an amount of nitrogen can be used for sweeping the permeation side producing a synthesis stream ($N_2/H_2 = 1/3$) ready for the final reaction step. If a sweep gas is used in the permeation side, then a packed bed membrane reactor can be used in both cocurrent or counter-current modes.

An interesting feature of packed bed membrane reactors is the possibility to operate them in a reverse flow mode, integrating the reaction and separation with the recuperative heat exchange inside the reactor. This operational mode is quite interesting for partial oxidation of methane (POM) (Smit et al. 2005). In normal POM systems, air and CH_4 feed streams have to be preheated to the reaction temperature, while POM reaction being only slightly exothermic, the external heat transfer between feed and exhaust is very expensive. Therefore, recuperative heat exchange is preferably carried out inside the reactor.

Although the tube in tube configuration is quite useful to work in lab scale and for proof of principle of membrane reactors, for industrial scale some other configurations need to be used in order to increase the membrane area per volume

of vessel used. In fact, the amount of hydrogen produced is directly related to the amount of membrane area installed in the reactor. Starting for the tube in tube configuration, a straightforward way to increase the membrane area in packed bed is the tube in shell configuration (Buxbaum 2002; Tosti et al. 2008).

Although the packed bed configuration is very advantageous and easy to operate, the production of thin membranes brought under the spotlight one of the disadvantages of fixed bed membrane reactors: the influence of bed-to-wall mass transfer limitations on the membrane area required. Briefly, as long as the hydrogen flux through the membrane is a limiting step, the effect of external mass transfer limitations such as the limitations to hydrogen transport between the bulk of the catalytic bed (where hydrogen is produced) and the membrane wall (where hydrogen is recovered) can be neglected. However, by increasing the membrane flux, the external mass transfer limitations became limiting and determine the extent of membrane area. This has been demonstrated both experimentally (Peters et al. 2008) and numerically (Gallucci et al. 2010). This important drawback has driven the research toward new reactor concepts such as micromembrane reactors or fluidized bed membrane reactors.

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Palladium-Based Membrane (Palladium Alloy Membrane)

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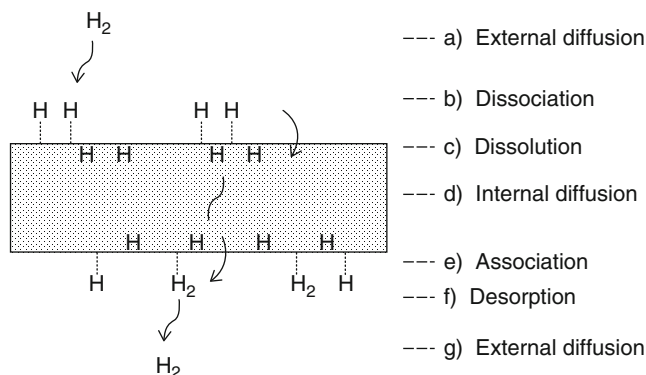
Palladium-based membranes have received a growing interest for the separation and purification of hydrogen from various resources (Paglieri and Way 2002; Yun and Oyama 2011; Gallucci et al. 2013). In addition, palladium membranes can be used as a palladium-based membrane reactor where the separation process is coupled with catalytic reactions. Palladium-based membranes have advantages of high hydrogen flux and exclusive permselectivity for hydrogen due to the unique permeation mechanism as shown in Fig. 1.

General Aspects

The developments in Pd and Pd alloys have been carried out for a long time (Buxbaum 1999; Grashoff et al. 1983; Holleck 1970). The most important problem associated with the use of pure Pd membranes is the hydrogen embrittlement phenomenon. Operation with hydrogen at a temperature below 300 °C and a pressure below 2 MPa leads to the nucleation of the β -hydride phase from the α -phase resulting in severe lattice strains. In this case a pure palladium membrane becomes brittle after a few $\alpha \rightleftharpoons \beta$ cycles (Hsieh 1989). Another important problem is the palladium surface poisoning, which can be more significant for thin metal membranes, by sulfur compounds (Edlund and Pledger 1994), CO (Amandusson et al. 2000), H₂O (Li et al. 2000), chlorine, carbon, unsaturated hydrocarbons, etc. In order to avoid hydrogen embrittlement and poisoning and reduce membrane cost,

Palladium-Based Membrane (Palladium Alloy Membrane),

Fig. 1 Solution-diffusion mechanism of hydrogen permeation through a palladium-based membrane (Yun and Oyama 2011)



palladium can be alloyed with other metallic elements such as Ag, Cu, Fe, Ni, Pt, and Y (Bryden and Ying 2002; Qiao et al. 2010; Uemiyama et al. 2007), or the palladium grains can be used in nanometer sized (Pacheco Tanaka et al. 2006).

Palladium Alloys

Among binary palladium alloys, Pd-Ag, Pd-Cu, Pd-Au, Pd-Ce, and Pd-Y exhibit higher permeabilities in comparison to pure Pd, according to Knapton that tested 25 μm thick alloys (Knapton 1977). $\text{Pd}_{90}\text{Y}_{10}$ has hydrogen permeability 3.8 times higher than pure Pd at 350 $^{\circ}\text{C}$.

Some interesting palladium alloys to avoid embrittlement are $\text{Pd}_{77}\text{-Ag}_{23}$ and $\text{Pd}_{70}\text{-Pt}_{30}$ (weight%) alloys since their critical temperature (T_c) for formation of the β -phase is around room temperature (Paglieri and Way 2002). Besides, Pd-Cu alloys do not show embrittlement even at low temperatures (Kulpatirpanja et al. 2005).

Pd-Cu, Pd-Au, Pd-Pt, Pd-Rh, and Pd-Ru alloys have been used for increasing the tolerance to sulfur (Paglieri and Way 2002; Morreale et al. 2004; Way et al. 2008). According to McKinley, a $\text{Pd}_{60}\text{Au}_{40}$ (mass%) is superior to a $\text{Pd}_{60}\text{Cu}_{40}$ (mass%) concerning poisoning by sulfur (McKinley and Nitro 1967). According to Morreale et al., face-centered cubic (fcc) Pd-Cu showed a decline of 0–10 % permeability when exposed to 1,000 ppm of sulfur, and body-centered cubic (bcc) Pd-Cu showed a decline of 99 % at the same sulfur content stream (Morreale et al. 2004). Thus, the final structure of the

palladium alloy is an important issue. In general, the sulfides of Pt, Ir, Rh, and Ru are much less stable than those of the Pd, and thus these elements show better tolerance to poisoning by sulfur.

Currently, novel Pd-based ternary alloy membranes are being studied (Peters et al. 2011, 2013).

Unsupported and Supported Membranes

Unsupported Pd-based membranes need to be thick self-standing films ($>50 \mu\text{m}$ thick) in order to have a minimum mechanical stability. The main drawback of these membranes is their low hydrogen permeance. Moreover, in the case of using an expensive membrane material, the cost of the whole membrane will be sharply increased by increasing the membrane thickness. Thus, there is a threshold between membrane mechanical stability and membrane thickness (and thus flux and costs). For this reason it is foreseen that the first industrially available membranes will be supported membranes. Supported membranes consist of a thin selective film deposited onto a support that provides mechanical stability. Thus, the hydrogen permeance of the membrane will be higher so that less membrane area is required and the whole membrane cost will be lower than that for unsupported membranes. However, in the total membrane cost, the cost of the support also becomes important. Especially when very thin film membranes are selected, the support pore size should be much lower and the surface much

smoother, so that its cost will increase. There are mainly two types of porous support materials: metallic and ceramic. Ceramic supports typically have better surface quality providing membranes with thinner selective layers. However, they are more fragile. Metallic supports are more robust than ceramic, but the commercial ones, mainly tubular, have lower surface qualities. Some research groups are developing hollow fiber supports (both ceramic and metallic) in order to increase the surface area to volume ratio and also improve the surface quality (Luiten-Olieman et al. 2012). In the case of the Pd-based membrane, support is metallic and is used at temperatures above the Tamman temperature of one of the metallic parts, common situation for high-temperature reforming reactions; it is necessary to position an intermetallic diffusion barrier layer between the metallic support and the metallic selective layer. In this case the materials used as barrier layer are ZrO_2 (Tarditi et al. 2013), YSZ (Sanz et al. 2011), TiO_2 (Li et al. 2008), CeO_2 (Qiao et al. 2010), and Al_2O_3 (Dardas et al. 2009).

Palladium Membrane Preparation

Common Pd-based layer deposition technologies include physical vapor deposition (PVD, including magnetron sputtering, thermal evaporation, or pulsed-laser evaporation), chemical vapor deposition (CVD or MOCVD), electroless plating (ELP), electroplating, and diffusion welding (Iniotakis et al. 1987). Each technology has its strengths and weaknesses; therefore, there is a trend of tailoring the deposition technology to the features of the support in order to obtain a suitable composite membrane. The most widely used preparation technology for dense metal layers is ELP due to its ability of covering supports with complex geometries, the simplicity of the required equipment, and its low cost (absence of electrodes or electrical source) (Mallory and Hajdu 1990). On the other hand, PVD magnetron sputtering is a very attractive deposition technology because it could provide thinner uniform



Palladium-Based Membrane (Palladium Alloy Membrane), Fig. 2 Palladium-based commercial tubular membranes manufactured by CRI/Criterion (<http://www.cricatalyst.com/>)

layers (down to only few nanometers), much lower than the thickness achieved with the ELP technique, with a controlled microstructure and composition across of these coatings. Other important advantage of PVD versus ELP is its environmental friendly operation, without producing waste liquids from chemical baths (Klette 2005).

Membrane Commercialization

There are various companies working in the commercialization of palladium-based membranes as reported by Gallucci et al. (2013); Figure 2 shows Pd-based tubular membranes manufactured by CRI/Criterion. As an example of industrial application and membrane scale-up, three commercial membranes from MRT, ECN, and NGK have been used in membrane reactors for methane steam reforming in a pilot plant for 20 m^3/h of hydrogen at Tecnimont KT (Italy) (Palo

et al. 2012); the membranes showed good performance over 1,300 h of testing and 70 cycles of start-up and shutdown with no signs of membrane degradation regarding hydrogen regarding hydrogen permeation properties.

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Palladium-Based Membrane Reactor

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In palladium-based membrane reactor a hydrogen separation process using palladium-based membranes is coupled with catalytic reactions. It has received a growing interest in recent years (Gallucci et al. 2011; De Falco et al. 2011; Gallucci et al. 2013). Membrane reactors are mainly used to carry out the reactions limited by the equilibrium conversion such as water gas shift (WGS) and so on. In fact, in a membrane reactor the separation capability of a membrane is utilized to improve the performance of a catalytic system.

General Aspects

There are two main generic approaches in Pd-based membrane reactors: selective hydrogen

separation (extractor) and selective hydrogen addition (distributor), as shown in Fig. 1.

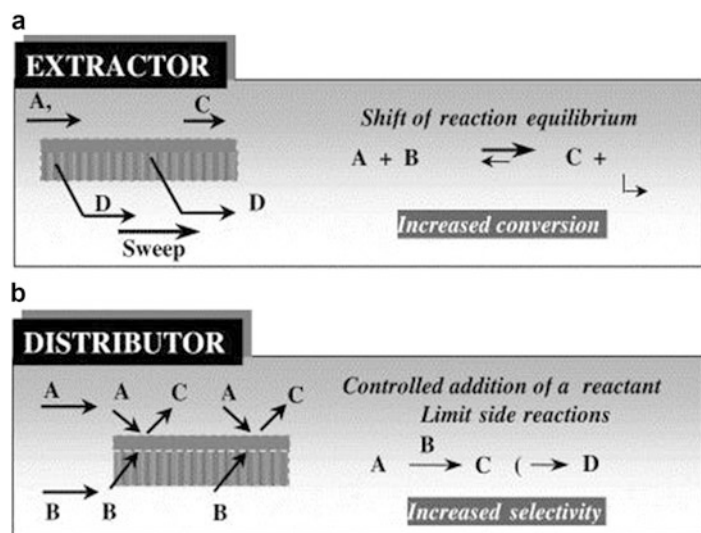
The extractor-type membrane reactor facilitates the in situ removal of hydrogen in the case of using palladium membranes. For example, for steam reforming reactions, H₂ yield and CO₂ product selectivity in traditional reactors are limited by thermodynamics. By selective removal of H₂ from the reaction side, the thermodynamic equilibrium restrictions can be overcome following the Le Chatelier's principle. Due to the shift effect, both high H₂ yields and high CO₂ selectivities can be achieved. Besides, this effect allows operation at milder reaction conditions in terms of temperature and pressure (Zaman and Chakma 1994). The distributor-type membrane reactor may use the Pd-based membrane to feed the hydrogen distributively in order to control the contact within reactants. For example, this reactor type can be used for Fischer–Tropsch synthesis reaction (Rohde et al. 2005).

In general, with respect to the traditional reactors, membrane reactors are able to:

- Combine chemical reaction and hydrogen separation in only one system reducing the capital cost
- Enhance the conversion of equilibrium limited reactions

Palladium-Based Membrane Reactor,

Fig. 1 Two approaches in membrane reactors: (a) extractor and (b) distributor (Julbe et al. 2001)



- Achieve higher conversions than traditional reactors operating at the same membrane reactor conditions or the same conditions, but operating at milder conditions
- Improve yield and selectivity

Hydrogen Production by Pd-Based Membrane Reactors

In the late 60s, Prof. Gryaznov proposed the use of Pd-based membrane reactor for dehydrogenation reactions (Gryaznov et al. 1970). Since then, dense Pd-based membranes and microporous silica membranes were studied for hydrogen production by membrane reactors. Pd-based membranes for H_2 production overcome all the other candidate materials due to the very high permeability and infinite perm-selectivity to H_2 . The most commonly studied reactions using Pd membrane reactor have been: methane steam reforming (Chen et al. 2008), methane dry reforming (Gallucci et al. 2008), partial oxidation of methane (Basile and Paturzo 2001; Cheng et al. 2009), and water gas shift reaction (Galuszka et al. 2012). Besides, reforming reactions using other sources were also

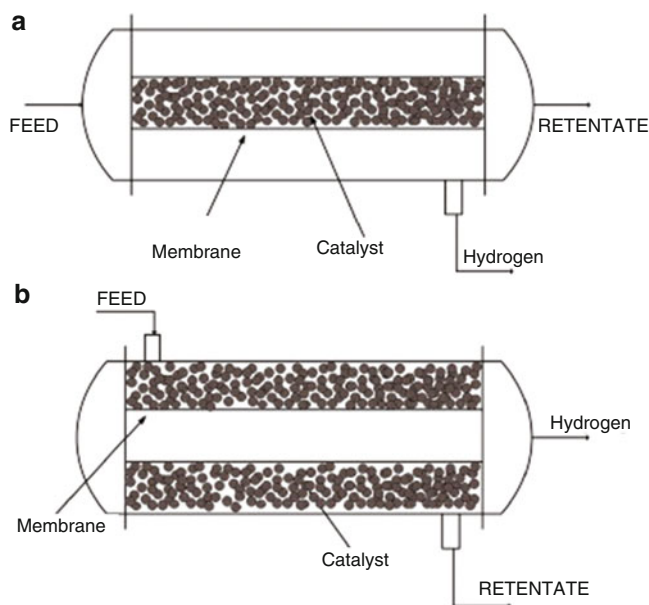
studied such as, steam reforming of ethanol and methanol (Gallucci et al. 2007).

Membrane Reactor Configurations

Different types of membrane reactors for hydrogen production have been proposed in the literature. Most of the previous work has been performed in packed-bed membrane reactors (PBMR); however, there is an increasing interest in novel configurations such as fluidized-bed membrane reactors (FBMR) and micromembrane reactors (MMR) especially because better heat management and decreased mass transfer limitations can be obtained in these reactor configurations.

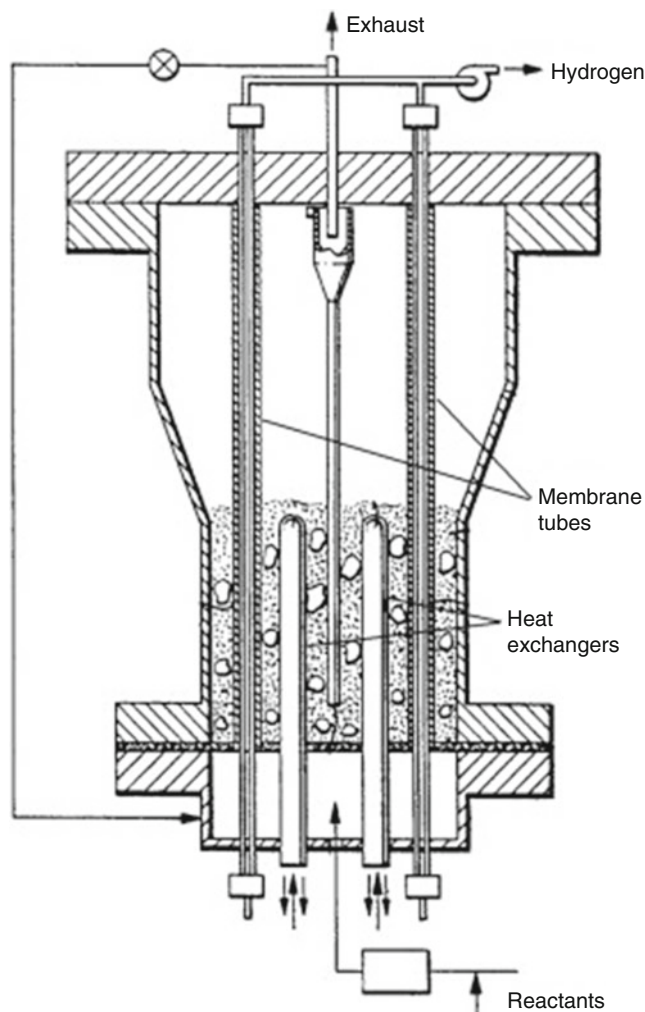
The PBMR configuration is the first and most studied configuration for hydrogen production in membrane reactors. This is because, the first studies on membrane reactors focused on the effect of the hydrogen permeation through membranes on the reaction system. Thus, it was straightforward to compare two packed-bed reactors (avoiding the complication of complex fluid dynamics such as

Palladium-Based Membrane Reactor,
Fig. 2 Packed-bed tubular membrane reactor configurations: (a) catalyst in tube and (b) catalyst in shell (Gallucci et al. 2013)



Palladium-Based Membrane Reactor,

Fig. 3 Schematic representation of a fluidized-bed membrane reactor for selective removal of hydrogen is presented (Adris et al. 1994)



in fluidized bed) in one of which a membrane was used. In a PBMR, the catalyst is confined in fixed-bed configuration and in contact with a Pd-based membrane. The most used PBMR configuration is the tubular one where the catalyst may be placed either in the membrane tube or in the shell side as shown in Fig. 2.

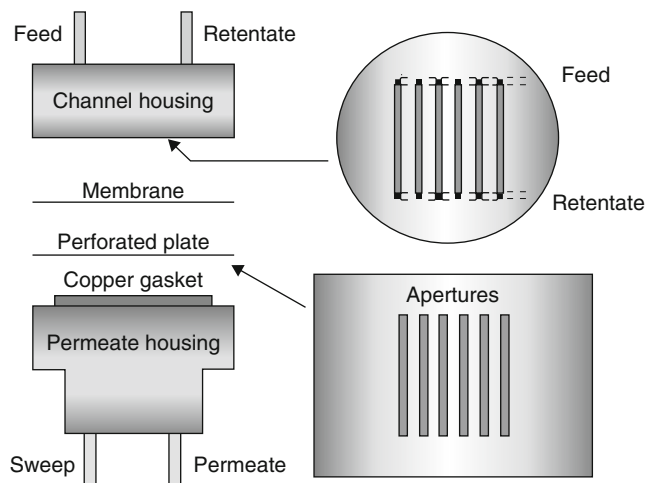
The FBMR configuration consists of a bundle of hydrogen selective membranes immersed in a catalytic bed operated in the bubbling or turbulent regime (see Fig. 3). Compared to PBMR configuration, the use of FBMR reduces the bed-to-wall mass transfer limitations

but also allows operating the reactor at a virtually isothermal condition (due to the movement of catalyst).

The MMR configuration is interesting due to: (i) improved mass and heat transfer owing to the reduction of the scale length in the microchannels; (ii) removal of mass transfer limitations (concentration polarization); and (iii) high degree of process intensification by integrating different process steps in a small-scale device. (Gallucci et al. 2013). The microchannel reactor configuration proposed by Bredesen and coworkers is presented in Fig. 4.

Palladium-Based Membrane Reactor,

Fig. 4 Schematic representation of the microchannel reactor configuration used by Bredeesen for Pd-based membrane tests (Mejdell et al. 2009)



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Palladium-Loaded Hollow Fibers: Application in Water Deoxygenation

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Palladium nanoparticles can be deposited on a hydrophobic porous polypropylene hollow fiber membrane, which preserves its hydrophobic nature (Lebedeva et al. 2006). Prior to the

deposition of palladium onto the membrane surface, hollow fibers should be cleaned with surfactants and organic solvents. Then, their outer surface is etched either by strong inorganic acids or by strong inorganic bases. The next step includes electroless deposition of palladium by one of the two following methods: (1) reduction of palladium tetraaminochloride by hydrazine hydrate (initial membranes are Accurel Q3/2 and Accurel S6/2) and (2) reduction of palladium chloride or palladium acetate by methanol (Accurel Q3/2, Celgard X50) (Volkov et al. 2009). According to the computational analysis of the SEM images, surface porosity of the initial membranes (both Accurel Q3/2 and Celgard X50) slightly increases after pretreatment. All palladium appears to be localized on the outer surface of the hollow fiber membranes. The deposition method (1) is characterized by a high deposition rate, and it provides a nearly dense palladium layer with thickness of 2–3 μm .

The slow wet-chemical deposition method includes the use of aliphatic alcohols (e.g., methanol) which serve as a reducing agent and as a solvent for palladium salts, and this process makes it possible to provide deposition of well-distributed fine palladium nanoparticles. In this case, loading of palladium is well below 20 $\mu\text{g}/\text{cm}^2$, and dimensions of nanoparticles tend to decrease with decreasing level of loading. The EDX and EXAFS observations reveal no other palladium-containing phases (e.g., oxides) and crystallinity of metallic palladium is proved by the XRD analysis. Dimensions of primary particles in their free state and in aggregates are estimated by the methods of X-ray analysis and SEM observations. Dimensions of primary palladium particles range from 10 to 40 nm, and dimensions of their aggregates vary from 200 nm to tens of microns.

Palladium nanoclusters can catalyze DO hydrogenation, thus providing *water deoxygenation by catalytic membranes*, even though the loading of palladium is as low as 5 $\mu\text{g}/\text{cm}^2$. The estimated surface porosity is $(12 \pm 1) \%$, $(17 \pm 2) \%$, and $(17 \pm 3) \%$ for initial Celgard X50, pretreated membrane, and Pd-loaded membrane

(5.4 $\mu\text{g}/\text{cm}^2$ Pd), respectively. For the sample containing $\approx 39 \mu\text{g}/\text{cm}^2$ of Pd, surface porosity cannot be estimated by the computer-aided SEM image processing because the deposited palladium totally occupies the entire structure of porous membranes. Palladium can be deposited either onto individual hollow fiber membranes or onto the surface of membranes within a membrane module. Hence, commercially available membrane module (Liqui-Cel[®]) can be coated integrally as delivered, without any disassembly. Reduction of DO down to its concentration of 10 parts per billion (ppb) and lower is feasible using catalytic membrane reactors based on palladium-loaded porous hollow fibers.

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PALS

- [Polymeric Membrane Characterization by PALS](#)
- [Positron Annihilation Lifetime Spectroscopy \(PALS\)](#)

Paper Industry and Membrane Operations

- [Pulp and Paper Industry and Membrane Operations](#)

Paper Machine Circulation Water and Membrane Operations

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In papermaking great amounts of water are used. First, pulp is diluted with water to form a feasible solution for mixing of the different additives, which improve quality of the produced paper. After that the pulp solution is diluted with water to the consistency, in which it can be spread over the paper machine wire section to form paper. At the wire section, water is removed from the paper web by gravity, low pressure, and pressing the paper web between large rolls. The water collected from the wire section of the papermaking process is called paper mill white water. The circulation of the paper machine white water as such in pulp dilution enables great savings in the amounts of the used freshwater. However, papermaking is still after that a really water-intensive process and the need of freshwater is great. When white water is purified with membranes, it can compensate freshwater and improved water efficiency is achieved. Ultrafiltered white water can be used, for instance, in wire section showers, dilution of chemicals, and in sealing and in lubrication of pumps (Nuortila-Jokinen and Nyström 1996; Nuortila-Jokinen et al. 1999; Huhtamäki 2002).

The internal purification of paper machine white water is attractive, because its volume is one of the greatest of the paper mill effluents. The most significant benefits in water savings can be achieved by treating the streams having the greatest volumes. Clear filtrate, which is paper mill white water clarified by disc filtration or microflotation to recover fiber and to remove most of the suspended solids, can constitute more than half of the total effluent load of a paper mill. To enable the use of clear filtrate at the wire section showers, it has to be free from solids, which could block the shower pipes. Ultrafiltration membranes can produce permeate,

which is free from solids. Moreover, compared to the use of freshwater or flotated clear filtrate, the use of ultrafiltered clear filtrate can reduce slime problems in the shower pipes and potential web breaks or web defects originating from microorganisms and the consumption of biocides, because ultrafiltration removes bacteria and reduces the amount of colloidal bio-organism nutrients. Ultrafiltration reduces also the amount of dissolved and colloidal substances, such as hemicelluloses, starch and resin, and fatty acids, which could cause disturbances in the papermaking process and deteriorate the end-product quality. The use of ultrafiltration can also decrease the consumption of fixatives, because the cationic demand of ultrafiltered process water is significantly lower compared to non-treated process water (Nuortila-Jokinen et al. 1999; Huhtamäki 2002; Huuhilo et al. 2002; Brady 2003; Kreutzman and Sutela 2004; Sutela et al. 2006). When the ultrafiltration permeate is nanofiltered, its COD, conductivity, and anionicity can be significantly reduced, and the nanofiltration permeate can be used as warm freshwater at the mill site.

Ultrafiltration is used to enable the recycling of the clear filtrate at several paper mills. For instance, at UPM-Kymmene Corp. Tervasaari paper mill (Valkeakoski, Finland), CR filters and UF membranes are used to purify 120 m³/h of white water for reuse at wire and press section showers. At SAPPI Ltd Kirjaniemi Paper Mill (Lohja, Finland), 425 m³/h of white water is purified with CR filters and UF membranes for reuse at wire section showers and chemical dilutions (Sutela 2008). At Arctic Paper Munkedal mill (Sweden), tubular UF membranes are used to purify the white water for reuse at wire section showers (Hepp et al. 2005).

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Paper Mills and Membranes

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Most of the membrane processes at paper mills aim to decrease in fresh water intake, decrease in production of waste waters, and purification of waste waters. Papermaking consumes high volumes of water. In a modern paper mill, the water consumption can be less than 10 m³ water per one ton of produced paper, but in older mills the water consumption can be significantly higher. The use of membrane processes enables the reduction of water consumption to values below 10 m³ per one ton of produced paper.

In efforts to decrease the water consumption of paper mills, the greatest benefits can be achieved by treating and recycling the effluent streams with

the greatest volumes. For instance, ultrafiltration of paper machine clear filtrate (paper machine white water), which can constitute more than half of the total effluent load of a paper mill, enables significant reduction in fresh water use. Ultrafiltration removes suspended solids and microorganisms and reduces the amount of organic dissolved compounds (lignin, hemicellulose, etc.). Ions bound for instance to fibers are also removed. The clear filtrate purified with ultrafiltration can be used at wire section showers, as sealing water, and in dilution of wet end chemicals. Nanofiltration removes, depending on the treated water, conditions and the used membrane from 70 % to 90 % of dissolved organic compounds (COD, TOC), color, and lignin degradation products. In addition, nanofiltration can retain multivalent ions. Nanofiltered paper machine white water can be reused as warm fresh water. The membrane processes treating the paper machine white waters and clear filtrates are operated with high shear rate modules (CR-filter, VSEP-filter), tubular modules, and conventional spiral-wound modules (Linpac 2006; Kreutzman and Sutela 2004; Sutela 2008).

The use of great volumes of water in a manufacturing process leads to the production of great volumes of waste waters. Membrane processes are used also in the treatment of paper mill waste waters to upgrade the purification result of biological waste water treatment and to reduce the amount of scarcely biodegradable compounds in the effluents, which are going to end up to the biological treatment before they are discharged. For instance Eltmann newsprint mill of Papierfabrik Palm has used since 1999 nanofiltration to recycle the effluent from the external biological treatment plant back to the paper mill processes. The concentrate is precipitated with lime to increase its biodegradability and led back to the biological treatment plant (Schirm et al. 2001). Some paper mills have also membrane bioreactors as an essential part of their waste water purification systems (Ramaekers et al. 2001).

In addition to the membrane processes aiming to the decrease of water consumption and environmental load of paper mills, there are also

processes, which aim significant improvements in material efficiency of the mills by recovering valuable compounds from the effluents for reuse at the processes. A great example on a membrane process, which improves material and cost efficiency of the papermaking process and also decreases the environmental load caused by the mill, is ultrafiltration of coating color effluents. Coating effluents form only a small part of the total mill effluents, but they have a strong color and they contain high amount of solids and sticky compounds. Thus, they are not easy to handle in the conventional waste water treatment plant. When the effluent is concentrated with ultrafiltration, the concentrate has a composition close to the original coating color and it can be recycled back to the coating process. When the valuable TiO_2 pigments are used in paper coating, the pay-back time of the ultrafiltration process is typically only around a year. The permeate can be used as sealing water, as washing water, as shower water, as slurry dispersant, or in the dilution of chemicals. The treatment of the coating color effluents is beneficial to do with high shear rate filtration modules (VSEP and CR-filters), because they enable concentration to high dry solid content (even up to 60 %) (Jönsson et al. 1996; Alho et al. 1998; Singh et al. 1999; Lipnizki 2008; Anon. 2013).

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Paper Pulp Production and Membrane Operations

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A conventional kraft pulp mill can use up to 40 m³ of fresh water to produce 1 ton of chemical pulp (Reeve and Silva 2000). Only about half of the wood is converted to pulp in the pulping process, and the rest of it is dissolved during the process. Thus, great volumes of effluent, which contain

compounds dissolved from wood and chemicals used in pulp-making process, are produced at pulp mills. Nearly half of the water consumed in the pulp mill is used in the pulp bleaching process, and bleaching effluents cause a major part of the color and a significant part of the chemical oxygen demand (COD) load of total pulp mill effluent. They also have high biological oxygen demand (BOD), and, depending on the bleaching chemicals used, they might contain adsorbable organic halogens (AOXs). Efficient purification of the bleaching effluents enables significant decrease in the environmental load caused by the pulp mills.

At pulp mills membrane filtration can be used in treatment of different effluents and process streams to enable water reuse or decrease in environmental load of the mill. The most typical ultrafiltration membrane application at pulp mills is the treatment of alkaline bleaching plant effluents. Ultrafiltration can reduce the color, BOD, COD, and AOX load of bleaching effluents, and it makes it possible to reuse the purified effluent, for example, as washing water. Ultrafiltration prior to the biological treatment also improves the purification result possible to achieve in the biological treatment, because ultrafiltration removes slowly degrading high molar mass lignin compounds and decreases the amount of chlorinated compounds, which are resistant to attack by most microorganisms. The concentrate of the ultrafiltration process is generally burnt in the recovery furnace where the cooking chemicals are recovered. If the mill produces several pulp products, mill effluent quality might vary depending on the products manufactured at the mill. The use of membranes enables high and stable removal of solids, regardless of changes in the effluent quality (Ekengren et al. 1993; Afonso and de Pinho 1995, 1997; Jönsson and Trägårdh 1990; Wallberg et al. 2001).

A real-life example, which is well reported in literature, is the ultrafiltration process used at Stora Enso Nymölla pulp mill (Sweden) which reduces the COD load of the mill effluent prior to its treatment in the activated sludge plant. The UF plant is based on tubular membranes. The total membrane area of the plant is 4,638 m². The ultrafiltration process has enabled

a COD reduction of about 50 % even with high volume reduction factors. The permeate is discharged to an activated sludge plant (Greaves 1999; Nordin and Jönsson 2008; Anon 2013b).

As already mentioned, pulp mill process waters and effluents are rich in compounds dissolved from wood. When the focus of forest industry is moving toward biorefining and toward utilization and also other parts of wood than cellulose, the use of membrane separation at pulp mills most probably increases, because membrane technology enables separation and recovery of the valuable hemicelluloses, lignin, and other compounds from process streams and effluents. There already are good examples, where ultrafiltration is used in recovery of lignin compounds from pulp mill. In Sarpsborg (Norway), at the mill of Borregaard Industries, lignosulfonates have been recovered from spent sulfite liquor for production of vanillin by ultrafiltration since the 1980s (Jönsson and Wimmerstedt 1985; Wagner 2000), and at Domsjö biorefinery (Sweden) lignosulfonates are recovered with ultrafiltration to be used as dispersing agent. At Domsjö mill ultrafiltration is used also in recovery of bioresin from wood (Hildingsson and Domsjö 2014).

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Parameter Estimation: Optimization of Membrane Operation

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Parameter estimation, in engineering applications, represents a problem which arises in modeling

and control when one wants to describe physical reality (e.g., behavior of a system) by a model.

Mathematically speaking, it is desired to determine values of model parameters, $\mathbf{p}$, which minimize the difference between the set of n measured data, $\mathbf{y}$, and the set of data, $\hat{\mathbf{y}}$, predicted by a model. This problem can be written as follows:

$$\min_{\mathbf{p}} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (1a)$$

$$\text{s.t. } f(\hat{\mathbf{y}}, \mathbf{p}) = 0 \quad (1b)$$

where Eq. 1b stands for the model, in general a set of equations of different nature (e.g., linear, nonlinear, dynamic, stochastic) which relates predicted behavior of a system with estimated parameters. If $f(\cdot)$ is linear and no other constraints for $\mathbf{p}$ exist, problem (1) has analytical solution. In other cases, one exploits numerical methods such as quadratic or nonlinear programming to solve the problem.

Objective function (1a) represents the so-called least squares estimation cost, and it is recognized in statistics as a maximum likelihood estimation under assumption of normal distribution of measurement error.

Parameter estimation finds its applications in a field of membrane engineering and processes. These include nonlinear estimation of parameters of pervaporation (Cao and Henson 2003), reverse osmosis (Chatterjee et al. 2004), and modeling and control of other membrane processes (Selby and Shannon 2009; Madyastha and Prasad 2011).

Problem of parameter estimation is closely related to finding of intervals of confidence for estimated parameters. In principle, this problem is based on identifying the sensitivities of estimated parameters to observed data and was treated in study of gas permeation in polymers by (Scheichl et al. 2005).

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Partial Least Square Regression (PLSR)

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PLS approach was originated around 1975 by Herman Wold for the modeling of complicated data (Wold et al. 2001). PLS can be defined as a multivariate linear regression methodology, based on the decomposition of the data, into a set of orthogonal components or latent variables (LVs) (Kourti and MacGregor 1995; MacGregor et al. 2005; Metsämuuronena et al. 2002). PLS is recognized as a robust method with a strong statistical basis able to analyze data with noisy, collinear, numerous variables and even missing data points in both the input ($\mathbf{X}$ matrix) and output ($\mathbf{Y}$ matrix) data sets. An important aspect of this technique is that the output data structure guides the decomposition of the input data in a way that the respective orthogonal components explain as much as possible of the

covariance between the input and output (Santos et al. 2007).

As mentioned above, PLS links the input and the output matrices with “new” variables that are estimated as a linear combination of the original variables or their rotation. These new variables called X-scores and denoted by t_a ($a = 1, 2, \dots$, LV) are given by the following equation:

$$t_{ia} = \sum_k W_{ka}^* X_{ik}; (\mathbf{T} = \mathbf{XW}^*) \quad (1)$$

where $\mathbf{W}$ is the weight matrix that relates the X-scores with each variables of $\mathbf{X}$. On the other hand, the input matrix $\mathbf{X}$ can be obtained from the linear combination between the X-scores $\mathbf{T}$ and the loading $\mathbf{P}$ in order to minimize the X-residuals $\mathbf{E}$ (Eq. 2):

$$X_{ik} = \sum_a t_{ia} p_{ak} + e_{ik}; (\mathbf{X} = \mathbf{TP}' + \mathbf{E}) \quad (2)$$

Then, the output matrix $\mathbf{Y}$ can be obtained by means of the following equation:

$$Y_{im} = \sum_a c_{ma} t_{ia} + f_{im}; (\mathbf{Y} = \mathbf{TC}' + \mathbf{F}) \quad (3)$$

where $\mathbf{C}$ is the weight matrix that relates the X-scores with each variable of $\mathbf{Y}$; meanwhile, f_{im} represents the deviation between the observed and modeled responses and comprises the elements of the Y-residual matrix, $\mathbf{F}$.

Finally, the multivariate regression model can be obtained combining Eqs. 1 and 3:

$$\begin{aligned} Y_{im} &= \sum_a c_{ma} \sum_k W_{ka}^* X_{ik} + f_{im} \\ &= \sum_k b_{mk} X_{ik} + f_{im}; (\mathbf{Y} = \mathbf{XW}^* \mathbf{C}' + \mathbf{F} = \mathbf{XB} + \mathbf{F}) \end{aligned} \quad (4)$$

The PLS regression coefficients, b_{mk} ($\mathbf{B}$), can be written as

$$b_{mk} = \sum_a c_{ma} W_{ka}^*; (\mathbf{B} = \mathbf{W}^* \mathbf{C}') \quad (5)$$

The line obtained by linear regression of that swarm of data points, in the direction of maximum

variance, is the first latent variable (LV). In other words, it captures the main trend in the data set. Then, another linear regression is performed in the second direction of maximum variance but keeping in mind that this direction should be orthogonal to the first. This corresponds to the second LV. The remaining LVs are obtained accordingly (Santos et al. 2007).

In any analytical application, data are usually processed before using PLS. Results of projection methods, such as PLS, depend on the scaling of the data. With an appropriate scaling, one can focus the model on more important Y-variables and use experience to increase the weights of more informative X-variables (Erikson et al. 2006). The main techniques to preprocessing data are scaling to unit variance (UV), where the variable is centered and scaled to “unit variance,” and standard normal variate (UNV) that is the same as UV, but the variable is not centered, then the standard deviation is computed around 0.

In any empirical modeling, it is essential to determine the correct complexity of the model. Considering numerous and correlated X-variables, a substantial risk exists for “over-fitting” that means a well-fitting model with little predictive power (Wold et al. 2001). Cross-validation (CV) is a practical and reliable way to test the predictive significance (Höskuldsson 1996). Basically, in CV, the data are divided in groups followed by the development of parallel models that are evaluated with the differences between observed and predicted Y-values. In the evaluation, the observations are kept out of the developed model, while the response values (Y) are predicted and compared with the observed values. The procedure is repeated several times until every observation has been kept out. The sum of squares of these differences is computed and collected from all the parallel models to form the predictive residual sum of squares (PRESS), which estimates the predictive ability of the model (Wold et al. 2001). Finally, the model with the number of components giving the lowest PRESS is used. The ability of the model can be summarized using the R^2 that is the fraction of the sum of squares (SS) of Ys explained by the current

component and Q^2 (cross-validated R^2) which is the fraction of the total variation of the Ys that can be predicted by a component. The selected model needs to be validated before using it to understand or to predict new events. The best validation involves the use of new X-values also known as validation set, but an independent and representative validation is rare (Wold et al. 2001). In the absence of a real validation set, the best solution is to use a cross-validation approach which simulates how the model predicts new data well and model reestimation after data randomization which estimates the chance (probability to get a good fit with random response data).

The PLS applications have been reported in three principal areas: quantitative structure-activity relationship (QSAR) modeling, multivariate calibration, and process monitoring and optimization (Wold et al. 2001). This approach can be applied in membrane processes in order to correlate operating conditions as well as membrane characteristics (X matrix) with several response variables (Y matrix) such as permeate flux, selectivity, etc.

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Partial Pressure Profile

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In the field of *Membrane Technology*, the partial pressure profiles mostly refer to pressure profiles of a key species of interest established within a membrane device and/or through the membrane itself.

Concerning the partial pressure profile within membrane devices, they can be evaluated by numerical techniques like, as an instance of the most common one, computational fluid-dynamics simulation, implementing the momentum, energy, and mass conservation equations over the domain of interest together with the specific boundary conditions, which are usually defined at the

membrane surface in terms of known flux and/or concentration of the species involved in the process.

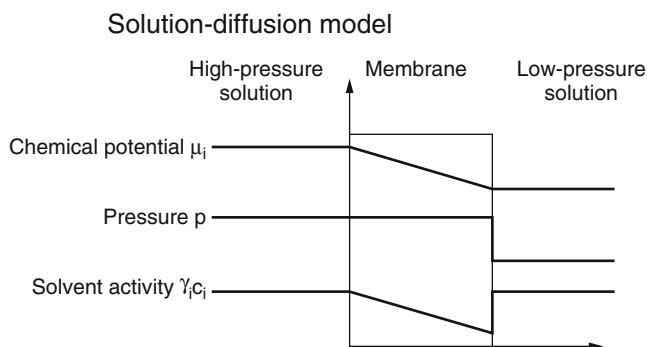
As for the partial pressure profile in membrane, they are usually determined by solving complex permeation models including several elementary transport mechanisms. Both complexity and type of the considered permeation model determine the shape of the specific transmembrane partial pressure profiles.

As instances of permeation models commonly used for dense and porous membranes, the profiles of chemical potential and pressure (for just one permeation species equivalent to the partial pressure) relative to the *solution-diffusion* model and the *pore-flow* model are sketched in Figs. 1 and 2 (Wijmans and Baker 1995).

Strictly speaking, since a pressure can be only defined for a fluid phase, partial pressure profiles can be basically established in porous membranes only, as the state of the permeating species inside dense membranes is actually an adsorbed/dissolved state.

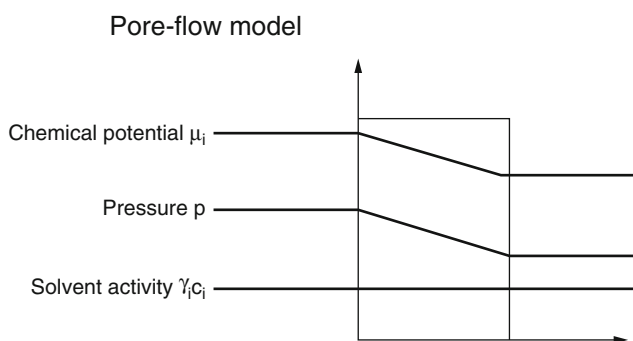
Partial Pressure Profile,

Fig. 1 Profiles of pressure, chemical potential, and solvent (membrane) activity according to the solution-diffusion model (Reprinted from Wijmans and Baker (1995) with the permission of Elsevier Science B.V. 1995)



Partial Pressure Profile,

Fig. 2 Profiles of pressure, chemical potential, and solvent (membrane) activity according to the pore-flow model (Reprinted from Wijmans and Baker (1995) with the permission of Elsevier Science B.V. 1995)



Nevertheless, it is also possible to represent the concentration profiles in dense membranes by the so-called equivalent partial pressure, which is the partial pressure of the permeating species being in equilibrium with its actual concentration in membrane at every position between the membrane surfaces on feed and permeate side (see, e.g., Caravella et al. 2008).

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Pd-Alloy Membrane Preparation Techniques

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Current Pd-alloy membrane technology comprises self-supported and mechanically supported composite structures. Self-supported membranes are usually in the form tubes or foils with thickness range of 50–100 μm with thicker membranes used at higher total transmembrane pressure. The H_2 flux, being in most cases inversely proportional to the thickness of the membranes, is too low for most applications to give a favorable cost-performance combination for most applications, apart from for small-scale H_2 production in the electronics industry. For broader use it is therefore necessary to develop membranes with a reduced thickness of the Pd layer, and for economically viable membranes a five to tenfold reduction in thickness is necessary. Research in recent years has therefore focused on the development of composite membranes consisting of a thin Pd-based separation layer on a mechanically strong support. The typical state-of-the-art composite Pd-alloy

membrane consists of a Pd separation layer of 2–10 μm thickness on a ceramic or metallic support.

Numerous reports exist describing different methods to fabricate such composite membranes. The most common are electroless plating, electroplating, CVD, sputtering, and various particle deposition techniques. Generally, for these methods, the thin Pd or Pd-alloy layer is prepared directly on the surface or inside the pores of the support. A lower thickness limit apparently exists, however, for which a dense and pinhole-free layer can be obtained during the direct deposition on a support. This thickness limit increases with increasing surface roughness and pore size in the support's top layer. Methods to circumvent support quality problems are developed and include support filling prior to plating, simply closing defects present after membrane manufacturing by selective deposition of Pd within them, or to manufacture the Pd selective layer independently of the support. In the latter process, a defect-free Pd-alloy membrane is first prepared by sputtering deposition onto the “perfect surface” of, e.g., a silicon wafer. In a second step, the membrane is removed from the wafer and transferred to a porous stainless steel support. This allows the preparation of very thin ($\sim 1\text{--}2\ \mu\text{m}$) defect-free membranes supported on macroporous substrates (pore size equals $\sim 2\ \mu\text{m}$).

The most frequently applied membrane manufacturing technique, electroless plating, has low cost and is applicable for large-scale production, but becomes increasingly more complex with the number of alloying elements. This is an important limitation in the membrane production as more advanced ternary or quaternary alloys may be needed to improve performance and stability (see “► [Ternary Pd-Alloy Membranes](#)”). Magnetron sputtering enables production of complex alloys with controlled stoichiometry in a controlled manner. In principle, the composition of the prepared film is homogeneous in the composition of the target applied, preventing thus the high temperatures required for alloying (550 $^\circ\text{C}$) that can be detrimental to the membrane integrity. However, magnetron sputtering is currently less developed for large-scale membrane production.

Pd-Based Composite Membranes

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Pd-based composite membrane (also called supported membrane). Pd-based membranes include pure palladium and palladium alloy membranes. They are highly permeable and almost 100 % permselective toward hydrogen (including its isotopes, i.e., deuterium and tritium). All gases and steams except for hydrogen will be rejected, yielding ultrapure hydrogen. The palladium-based membranes have been commercialized since 1960s, when Pd-Ag membranes were developed by Johnson-Matthey Co. and applied in hydrogen purification. They are often in forms of either tubes or foils and can be manufactured by cold drawing or rolling. For example, the cold rolling can be operated by (i) preparing a palladium alloy with certain composition by melting at high temperature, (ii) ingot casting, (iii) high-temperature homogenizing, (iv) hot and cold forging or pressing, and (v) repeated cold rolling and annealing (Shu et al. 1991). The membrane thickness is usually several tens of microns.

Because of the disadvantages of the conventional palladium-based membranes such as poor physical strength and high cost, a concept of composite or supported membrane was introduced, which comprises a thin layer of palladium or palladium alloy and a porous substrate. At first, the mechanical strength of the membrane can be greatly enhanced by the substrate. Secondly, the membrane thickness can be significantly reduced down to several microns, and the membrane permeance will accordingly increase because the membrane permeance is inversely proportional to the membrane thickness. Thirdly, the palladium consumption and the membrane cost can be greatly reduced because of the

reduction in membrane thickness as well as the decrease in the necessary membrane area.

However, the disadvantages of the composite membrane concept remain. It is difficult to avoid the membrane defects during membrane fabrication, and the maintenance of the membrane stability is also challenging because pinholes may appear along with the time on stream.

A photograph of various palladium-based composite membranes is exhibited in Fig. 1, and some Pd/Al₂O₃ membranes with a length of 1.2 m and a diameter of 13 mm are shown in Fig. 2.

Substrate Material

Due to their excellent chemical stability and broad market availability, porous ceramics and stainless steels are the most popular substrate materials for the composite palladium-based membranes. Principally, the porous ceramics have better surface properties and facilitate the membrane fabrication, but they are fragile and may lead to problems in membrane module construction. On the contrary, porous stainless steels can be welded and easy to connect with other metallic parts, whereas their pore size is often too large. Moreover, direct use of the porous stainless steels as substrate material of the palladium-based membranes will cause intermetallic diffusion problems. A ceramic coating on the porous stainless steels will not only improve the surface properties but also act as a barrier (Huang and Dittmeyer 2006). Since the defects such as big cracks and holes at the substrate surface may eventually lead to the defects in the membrane, it is important to test the surface pore size of the substrate before use, and for this purpose a capillary flow or bubble point method can be conveniently applied (Yu et al. 2010).

Membrane Preparation

Most of the commercialized self-support palladium-based membranes are made of palladium alloys such as Pd77Ag23, Pd60Cu40, Pd92Y8, etc. On one hand, pure palladium membranes suffer from hydrogen embrittlement

Pd-Based Composite Membranes,

Fig. 1 Photograph of various palladium-based composite membranes (http://www.njgaoq.com/products_detail/&productId=68.html)



Pd-Based Composite Membranes,

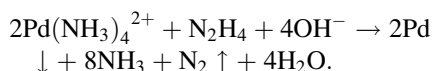
Fig. 2 Scale-up of the palladium-based composite membranes by GaoQ Functional Materials Co., Nanjing, China. (http://www.njgaoq.com/products_detail/&productId=70.html)



problem. On the other hand, the introduction of the other metals may improve the membrane permeability, physical strength, and/or poison resistance. In the case of the type of the composite membranes, the fabrication of the palladium alloy membranes is more difficult because of the difficulty in direct deposition of thin and defect-free palladium alloy layer on the porous substrate surface. Therefore, the palladium and the other metal(s) have to be deposited either sequentially or simultaneously, followed by a heat treatment for the formation of homogeneous palladium alloy. In general, the sequential deposition is the most common, and palladium is deposited at first.

Although there are many techniques that can be used in metal coating and deposition, such as

electroplating, chemical vapor deposition (CVD), magnetron sputtering, plasma thermal spray, and high velocity oxy-fuel (HVOF) spray, the electroless plating is almost the best as far as the deposition of palladium is concerned. Before plating, the substrate surface is often activated by a $\text{SnCl}_2/\text{PdCl}_2$ treatment to seed a layer of palladium nuclei as a catalyst. The palladium plating bath is often composed of PdCl_2 , Na_2EDTA , $\text{NH}_3\text{H}_2\text{O}$, and N_2H_4 , and the reaction during electroless plating is



During alloying of palladium and the other metal(s), a very high temperature (e.g.,

600–900 °C) and a long heating time are often necessary. However, such a severe heat treatment for such a thin metal layer may cause significant membrane defects and consequent poor membrane selectivity. Therefore, the composite membranes of pure palladium are still a good choice. In order to avoid the hydrogen embrittlement problem, the operating temperature of the pure palladium membranes should be above 300 °C, and below this temperature the raw hydrogen gas should not be fed to the membranes. After operation, the membrane should be purged with inert gas or vacuumed before cooling down. At a temperature below 300 °C, whether the hydrogen embrittlement occurs or not will depend on the partial pressure of hydrogen. For example, palladium will not be embrittled at 160 °C if the H₂ pressure is below ca. 2 bar, but above this pressure the H/Pd ratio will rapidly increase because of the formation of β -type palladium hydride, leading to a sudden expansion and a strong tension in palladium lattice (i.e., the so-called hydrogen embrittlement). To protect the composite membranes for longer operation life, rapid changes in hydrogen pressure and working temperature should be avoided anyhow.

Application

The applications of the palladium-based-composed membranes are almost the same as those of the conventional self-stand ones. Apart from the applications in hydrogen separation, purification, and recycling, they can be also used as membrane reactors for hydrogen-related reactions such as hydrogen production, hydrogenation, and dehydrogenation. In addition, they can be used even as membrane catalysts (Shu et al. 2009; Shi et al. 2010).

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Pd-Based Membrane: Exposure to Coal Gas

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Pd-based membranes have frequently been studied in membrane reactors for steam reforming (SR-MR) and water-gas shift (WGS-MR) reactions to simultaneously achieve a high methane conversion and production of pure H₂. A key feature of this process intensification is that such a membrane reactor would produce both a high-pressure CO₂ stream and high-purity H₂. Synthesis gas may also be produced by gasification of coal or biomass, enabling production of hydrogen from these important sources. Downstream processing of gasification effluents, i.e., separation or further reaction, is however more challenging than in the case of natural gas because of the wide range of possible impurities and by-products associated with the coal or biomass. Coal-derived synthesis gas can contain up to 15,000 ppm H₂S as well as COS (<0.1 %), NH₃ + HCN (<0.3 %), C₂ hydrocarbons, polyaromatic hydrocarbons (PAHs), halides (such as CH₃F, CH₃Cl at around 2 ppmv), heavy metals (such as Hg, Cd, Pb), tellurides (arsenides, selenium, antimony), alkali metals (Na, K, Ca), phosphorous, tars, and other unknown compounds, in concentrations varying with the source of the feedstock and the

gasification technology applied. Even though some field tests applying Pd-based membranes in actual coal-derived syngas have been performed, the reactivity of the majority of these compounds with Pd and its alloys is not known.

With current understanding, production of hydrogen from coal and other sulfur-containing sources is challenging for Pd-based membranes particularly due to their limited stability toward sulfur. Even a few ppm of sulfur in the gas reduces the flux drastically due to strong surface adsorption leading to reduced permeability, while higher concentrations (typically above 100 ppm depending on operating temperature) even lead to a complete deterioration of the membrane caused by formation of bulk Pd₄S. This has led to the development of a number of new alloys with higher sulfur tolerance (see entry “► [Ternary Pd-Alloy Membranes](#)”). Still, however, flux targets remain a challenge for these alloys in large-scale applications in the presence of sulfur impurities. For application of Pd-alloy membranes in coal-derived synthesis gas, sulfur needs thus to be removed by processes such as ZnO beds and hydrodesulfurization. This desulfurized synthesis gas may still contain trace levels of H₂S, and it is therefore important to assess the stability of Pd-alloy membranes under long-term exposure to trace levels of H₂S and to determine the upper acceptable H₂S level.

Pd-Based Membrane: Scale-Up

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Pd-based membrane technology is currently the standard for small-scale H₂ production (~0.25–150 Nm³/h) in the electronics industry as they can provide hydrogen to nine-nines purity, meeting the most stringent requirements for semiconductor fabrication processes. The technological standard for the production of ultrahigh purity

hydrogen is based on self-supported rolled foils or drawn tubes with thickness range of 50–100 μm. To increase cost-effectiveness compared to alternative technologies and processes, driven by the prospected use of hydrogen as an energy carrier, composite membranes with a reduced thickness of the Pd layer on a mechanically strong support are being developed. Here, the most frequently applied membrane-manufacturing technique, electroless plating, has low cost and is applicable for large-scale production; see Pd alloy membrane preparation techniques. Along this route, tubular composite membranes on porous metal supports have been developed by several companies, like Shell/CRI-Criterion, Pall Corporation, and Plansee/Linde for application in membrane-intensified steam reformer concepts. CRI Criterion currently produces membranes of ODs up to 2 in. and lengths up to 24 in. In addition, tubular membranes on ceramic support for application in WGS membrane reactors are offered on a pre-commercial basis by ECN/Hysep[®]. These modules, currently with membrane area up to 0.5 m², are only suitable for hydrogen separation. The nominal capacity of the largest membrane module equals 3.5–6 Nm³·h⁻¹, based on the obtained hydrogen flux applying reformat with 33 % H₂, an inlet pressure of 25 bar and H₂ outlet pressure of 4 bar.

For successful commercialization of Pd-based membranes, the membrane must have sufficient permeability, selectivity, robustness, and durability in relevant environments. Therefore, many companies and research institutes are as well working on pilot projects to demonstrate the technical feasibility of the Pd membrane technology. Although this effort is still mainly limited to laboratory-scale membranes or modules, some new (pre)commercial membrane modules have been successfully applied in pilot plant and industrial facilities. Tokyo Gas uses plate-type membranes incorporating Pd-based foils supported on stainless steel carriers in their 40 Nm³/h-class membrane reformer, and a membrane reforming pilot plant with 20 Nm³/h of hydrogen capacity has been constructed by Kinetics Technology in Italy to investigate different types of Pd-based membranes.

Pd-Based Tubular Membrane Reactor

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A *Pd-based tubular membrane reactor* consists of two concentric tubes where the internal one is the metallic membrane separating the two reactor sides, that is, the reaction and permeate volumes. The reaction side can be the core of the inner tube or the annular volume between the two tubes. The Pd-based membranes are used since they are permeable only to hydrogen. Therefore, such a reactor will be mainly evaluated on two performance parameters: feed conversion and hydrogen recovery on permeate side.

A reactor having a prevalent geometrical development along a specific direction is known as tubular reactor. Its most common cross section is the circular one even though other sections such as square, rectangular, etc., are possible. Thus, a cylindrical surface mostly delimits such a reactor and two circles define the entrance and exit surfaces.

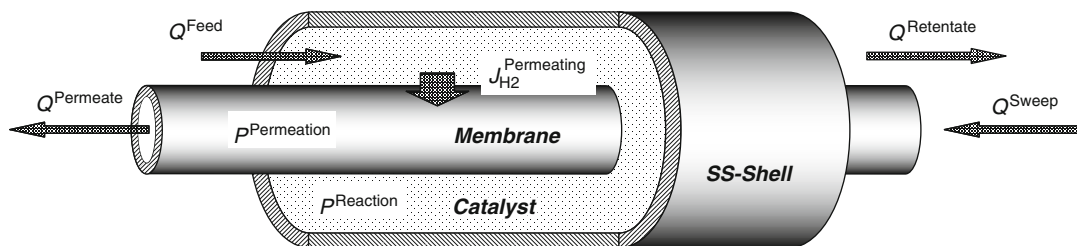
Such a tubular reactor with a circular cross section is commonly used both industrially and at a lab scale. This configuration allows the pressure on the reactor surface to be uniformly distributed, a very important issue for industrial application where the pressure can be really high; in some cases (see ammonia synthesis), the reaction pressure reaches 600–1000 bar. This reactor is commonly used in the laboratory for its cylindrical symmetry which allows to reducing the complexity of the equation set for mass and energy balance. Often, in a first approximation, radial and axial diffusions of mass and energy are neglected, and the resulting mathematical model consists in an ODE (ordinary differential equation) system of the first order whose resolution is much simpler than that of PDE (partial differential equations) system of the second order necessary for the mathematical description in the absence of cylindrical symmetry and radial and axial

diffusions. This reactor model, known as plug flow reactor (PFR), is the most common experimental investigated since its mathematical description consisting in a first-order ODE set, as above said, is the simplest one from a fluidodynamics point of view after the continuous stirred tank reactor.

The reactor diameter ranges from a few centimeters to meters also depending on the exothermicity/endothermicity of the reaction, in other words on the necessity of heat exchange/provision. Often, industrial reactors operate in adiabatic conditions, but in some cases the heat request by reaction is so high that energy has to be provided in order for the reaction to precede; in these cases small diameter is preferred to the higher one.

The simplest *Pd-based tubular membrane reactor* utilized the various advantages (cylindrical symmetry, no radial and axial diffusions) of a plug flow reactor on reaction side; this condition is also valid for the permeate volume. This membrane reactor (MR) model is mathematically described by a first-order ODE set. The two streams in the reaction and permeate volumes can be in co- or, as shown in the next figure, countercurrent configurations. The permeation driving force, the difference between the square root of hydrogen partial pressure on reaction and permeation sides, of a co-current tubular MR is the highest at the entrance and it reduces along the reactor length; if the reactor is really long, this difference becomes null. The permeation driving force of a countercurrent tubular MR is more distributed along the reactor length (Barbieri and Di Maio 1997). Therefore, countercurrent flow configuration results in a higher performance in terms of, e.g., reaction conversion and hydrogen recovery. The countercurrent configuration requires a shooting method for the numerical solution of the ODEs set. Equation 1 shows an example of an ODE system for an MR operating in steady state (Fig. 1):

$$\begin{aligned}
 -\frac{dF_i}{dz} + [\text{Generation by reaction}] \\
 - [\text{Permeation through the membrane}] \\
 = 0
 \end{aligned} \tag{1}$$



Pd-Based Tubular Membrane Reactor, Fig. 1 Scheme of Pd-based membrane reactor

The choice about the reaction volume as the one inside the core of the membrane or in the annular space between the two tubes depends on several factors, e.g., contact between the catalyst and membrane (can damage the membrane since this is a few microns thin) and heat transfer from the energy source and reaction. The heat transfer is more efficient (Marigliano et al. 2001) if the reaction takes place in the annular space since the resistance in this case is concentrated in the external tube and in the gas films around it. In the other case, the overall heat transfer coefficient is lower since the energy has to be transported through the permeation volume too.

Different reactor configurations and geometries also including radial and axial diffusions are often operated also at lab scale for analyzing the effect related to the mass and energy diffusive transport. The following Eq. 2 shows the complexity of PDE set of a two-dimensional second-order mathematical model written down for a tubular MR operating in steady state:

$$\begin{aligned} & \text{Diffusivity}_{i,z} \frac{\partial^2 p_i^{\text{ReactionSide}}}{\partial z^2} \\ & + \text{Diffusivity}_{i,r} \frac{\partial^2 p_i^{\text{ReactionSide}}}{\partial r^2} + R_{\text{gas}} T_{r,z}^{\text{ReactionSide}} \\ & \left(\frac{\partial N_{i,z}^{\text{ReactionSide}}}{\partial z} + [\text{Generation by reaction}]_{r,z} \right) = 0 \end{aligned} \quad (2)$$

Models for more complex reactor configurations and geometries also including radial and axial diffusions are reported in (Barbieri et al. 2008a) and characterized by first- and second-order PDE set.

Two more aspects have to be discussed for an MR: the concentration gradients, more known as concentration polarization, and the permeation reduction owing to the presence of some gases since both reduce the membrane performance.

The permeation is a mass transport happening at a surface – the one delimited by the membrane – and when it is selective creates a variation in the composition of species in the film close to the membrane itself. This variation will spread with a finite – not infinite – velocity; this means a concentration profile is created in the orthogonal direction at the membrane surface. The concentration profile is physiological in any membrane separation and its breadth depends on membrane selectivity and permeance. The higher the selectivity and permeance, the higher the concentration profile (Caravella et al. 2008, 2009; Boeltken et al. 2013). The presence of a concentration gradient reduces significantly the driving force for the permeation, that is, function of the partial pressure at the membrane surface and not the one in the bulk of the reaction and permeation phases.

The adsorption of some species such as CO and H₂S (Gade et al. 2011; Morreale et al. 2004; Kulprathipanja et al. 2005; Braun et al. 2012; Kajiwarra et al. 1999; Gabitto and Tsouris 2009; Chen and Ma 2010; Iyoha et al. 2007) on the membrane surface causing the reduction in the number of metal surface sites for hydrogen adsorption is a fundamental step for hydrogen permeation. This phenomenon, known in catalysis as poisoning of catalysts, follows the same adsorption laws, e.g., the Langmuir one (Barbieri et al. 2008b). It results in a significant increase of permeation resistance and similar

permeance reduction (Caravella et al. 2010). Both concentration gradients and inhibition by chemical species have to be taken into account for a proper evaluation of hydrogen permeation (Caravella et al. 2010, 2011; Barbieri et al. 2011) and hence membrane reactors performance.

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Pd–Cu Alloys for Hydrogen Separations

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Pd–Cu alloys have been widely studied as a hydrogen separation membrane because they do not show embrittlement even at low temperatures (Kulprathipanja et al. 2005; Miller et al. 2008). Studies by Morreale et al. have shown that the face-centered cubic (fcc) phase is more resistant to sulfur than the body-centered cubic (bcc) phase

(Morreale et al. 2004). In transient experiments, the fcc Pd–Cu composition showed a decline of 0–10 % when exposed to 1,000 ppm of sulfur, while a bcc Pd–Cu composition had a decline of 99 %. Studies by Pomerantz and Ma (Pomerantz and Ma 2009) confirm these results for Pd–Cu compositions of 8, 18, and 19 wt.% Cu, with permeance losses of 80 % at 500 °C (773 K). They further showed that the loss was partially reversible by hydrogen treatment. A recent study by Howard and coworkers (O'Brien et al. 2010) shows that Pd exposed to 1,000 ppm sulfur at 350 °C (623 K) corrodes over a period of hours to form a thick (6.6 μm) PdS₄ layer, probably by an autocatalytic process. In contrast a Pd₄₇Cu₅₃ alloy forms a thin (~ 3 nm) Pd–Cu–S layer. Although this layer cannot dissociate hydrogen or is impermeable to hydrogen, it does protect the bulk from sulfidation and could be removed by a hydrogen treatment.

The alloying of Cu with Pd increases the resistance for the α to β phase transition in Pd–H system. Moreover the phase transition in the Pd–H system is eliminated even at room temperature by adding more than 8 wt.% Cu in Pd (Karpova and Tverdokskii 1959). McKinley (McKinley et al. 1969) studied the permeation characteristics of Pd–Cu alloys with different compositions. The H₂ permeabilities of various alloys are shown in Table 1. Out of all other Pd–Cu alloys, the Pd₆₀Cu₄₀ shows the highest permeability which corresponds to the ordered β -phase in Pd–Cu system (McKinley and US. Patent 3, 439, 474 1969). In contrast, it is reported that Pd₄₇Cu₅₃ (mol%) alloy has the highest hydrogen permeability at 350 °C among

the Pd–Cu alloys (Yuan et al. 2007; Yang et al. 2007; McKinley et al. 1969; Roa et al. 2002) and is comparable in its hydrogen permeability to pure Pd at the same temperature. The solubility of Pd–Cu (20 % Cu) is five times smaller than that of pure Pd, which corresponds to the permeability behavior of that alloy (Sonwane et al. 2006).

In summary Pd–Cu (particularly Pd₆₀Cu₄₀) is the most promising composition; has the characteristics of having high hydrogen permeance, good sulfur resistance, robustness w.r.t. thermal cycling, and an excellent dimensional stability (small degree of swelling); is cheaper; eliminates warping and cracking; and avoids α to β phase transition in pure Pd (Gabbito and Tsouris 2009).

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Pd–Cu Alloys for Hydrogen Separations, Table 1 Permeabilities of Pd–Cu alloys with different wt.% of Cu at 350 °C, 300 psig

wt.%	Permeability (Cm ³ /cm ² .s)
90Pd–10Cu	0.69
70Pd–30Cu	0.12
60Pd–40Cu	1.52
550Pd–45Cu	0.25
45Pd–55Cu	0.01
90Pd–10Cu	0.69

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Pectin Hydrolysis and Membrane Operations

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Hydrolysis of pectin can be carried out by pectinase enzymes that are classified into three main groups (Pilnik and Voragen 1993):

- Pectinesterases – catalyzing de-esterification of the methoxyl group of pectin
- Depolymerizing hydrolytic enzymes (including polymethyl-galacturonases and polygalacturonases) – catalyzing the hydrolytic cleavage of 1,4-glycosidic bonds
- Lyases – catalyzing the cleavage of glycosidic bond by transesterification

Among the pectin hydrolyzing enzymes, (endo)polygalacturonases (PG, E.C. 3.2.1.15.) play a key role in the process. Regarding the kinetics it was found that PG enzyme from *Aspergillus niger* was inhibited by its monomeric product, galacturonic acid. The Michaelis-Menten model completed with competitive product inhibition describes properly the process.

To avoid product inhibition in hydrolysis of pectin, the inhibiting product should be removed by, e.g., a membrane separation. Ultrafiltration membranes provide proper separation since the small inhibitory product molecule (galacturonic acid) can easily pass through the membrane and be removed continuously from the system, while the large molecules (substrate and enzyme) are retained by the membrane. The enzymatic

reaction and the membrane separation can be carried out simultaneously in the same setup, which is called membrane bioreactor (Belafi-Bako et al. 2007; Kiss et al. 2009). In this way higher yields and efficiency can be achieved.

Pectolytic enzymes have been used for long in the fruit processing industry to increase yields, to improve liquefaction and clarification (Pilnik and Voragen 1993), and moreover to produce D-galacturonic acid (monomer of pectin), which is an important compound, raw material in the food, pharmaceutical, and cosmetic industry to manufacture, e.g., vitamin C or acidifying, tensioactive agents.

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Pectins

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Pectin is a general term for various polysaccharides. According to a standard nomenclature (Nelson et al. 1977), pectic substances are a group of complex, colloid carbohydrate polymers which are present and recovered from plant tissues and consist of mainly galacturonic acid as monomer (Walter 1991). Regarding structure, three different pectic polysaccharides can be

distinguished: homogalacturonan (HGA) and rhamnogalacturonans I and II (RGs I and II).

HGA is a linear polymer consisting of D-galacturonic acid monomers. The backbone of RG I is built from rhamnose and galacturonic acid alternately, while the main bone of RG II is composed of linear oligogalacturonic acid sequences (eight to ten monomers), where various monosaccharides are coupled to, resulting in a complex, branching polymer. The galacturonic acid units may occur in a free acid form, esterified by methanol, or as a salt formed with Na^+ , K^+ , and NH_4^+ ; moreover it may contain acetyl groups coupled to the OH groups. The composition of pectins (galacturonic acid content, molecular weight, methylation, acylation degree, etc.) depends on the source, i.e., pectins from citrus fruits have low esterification degree.

Pectin is widely used as thickening, gelling, and emulsifying additive in food, cosmetic, and pharmaceutical industries (Walter 1991).

Cross-References

- [Pectin Hydrolysis and Membrane Operations](#)
- [Pectins](#)

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and separation (clarification, purification, and concentration). In the separation steps, membrane processes (mainly ultrafiltration) can be widely applied.

In the commercial pectin extraction process, citrus peels and apple pomace are used as raw materials. However pectin recovery from agro-wastes would be more beneficial, since it is not only important from the environmental protection point of view (waste minimalization), but it may contribute to the more economical production. The potential pectin-rich agro-wastes are, e.g. cocoa husks, sunflower head, peach pomace, peels of mango, etc. Recently wastes of berry fruit (red and black current, blackberry, elderberry, etc.) processing have been studied (Belafi-Bako et al. 2012).

Extraction of pectic substances can be carried out by hot aqueous (acidic or neutral) solution in high temperature. It takes quite long (appr. 10–12 h). To improve the process, microwave technique can be applied (Fishmann et al. 2006).

As a result of the extraction (from, e.g., the berry press cakes by boiling water), majority of the pectic polysaccharides can be obtained in the aqueous phase. *Ultrafiltration* can be used then to clarify the extracted solution, and the diluted aqueous pectin solution may be concentrated partly by membranes (e.g., *ultrafiltration*, or *nanofiltration*, or *reverse osmosis*) up to 5 % total solid substance (TSS), partly by evaporation up to 30 % TSS. Then pectin in powder form can be obtained from the concentrated pectic solution after precipitation with ethyl alcohol.

Pectins, Recovery of

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Pectins occur in the plant tissues; its recovery means a combined process involving extraction

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PEGylation

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PEGylation refers to the covalent attachment of one or more polyethylene glycol (PEG) chains to another molecule, typically a small therapeutic protein (Veronese and Harris 2002). The attachment of the PEG increases the hydrodynamic size of the protein, reducing the clearance by the kidney and significantly increasing the half-life of the protein thereby reducing the dosage level and frequency. PEGylation can also reduce the antigenicity of the protein, significantly reducing any adverse immune response (Veronese 2009). A variety of commercial PEGylated proteins are currently on the market (Table 1).

PEGylation is typically accomplished by reacting an activated form of the polyethylene glycol with available reactive groups on the surface of the therapeutic molecule. This includes the free amino groups on the amino acid lysine as well as the free sulfhydryl group on the amino acid cysteine. The N-terminal amino group and the C-terminal carboxylic acid can also be used for site-specific PEGylation.

One of the challenges in producing PEGylated therapeutics is the need to remove the unreacted protein and PEG, as well as any multiply PEGylated species, from the desired (typically singly) PEGylated product (Fee and Van Alstine 2006). A variety of chromatographic methods have been developed for the purification of PEGylated proteins including size exclusion chromatography, ion exchange chromatography, and hydrophobic interaction chromatography (Fee 2009).

There is also considerable interest in the development of ultrafiltration systems for the purification of PEGylated proteins. Molek and Zydney (2007) demonstrated the use of ultrafiltration to remove the unreacted protein, reaction by-products, and unreacted PEG from a desired PEGylated protein using a two-stage diafiltration process. The first stage used an electrically neutral membrane to remove the small unreacted protein, with the neutral PEG removed in a second stage using an electrically charged membrane that provided high retention of the charged PEGylated protein. Ruanjaikaen and Zydney (2011) used a charged ultrafiltration membrane to remove multiply PEGylated species from singly PEGylated α -lactalbumin, with the more heavily PEGylated species retained by the charged ultrafiltration membrane using a combination of size and electrostatic interactions.

PEGylation, Table 1 Examples of commercial PEGylated products

Commercial name	Protein	Manufacturer	Indication
Adagen	Bovine adenosine deaminase	Enzon	Severe combined immunodeficiency
Oncaspar	L-asparaginase	Enzon	Acute lymphoblastic leukemia
PegIntron	Interferon alpha-2b	Schering-Plough	Hepatitis C, hepatitis B
Neulasta	Granulocyte colony-stimulating factor	Amgen	Neutropenia
Pegasys	Interferon alpha-2a	Hoffman-LaRoche	Hepatitis C, hepatitis B
Somavert	Modified human growth hormone	Pharmacia-Upjohn	Acromegaly
Macugen	Pegaptanib sodium	Osi Pharmaceuticals	Wet macular degeneration
Cimzia	Monoclonal antibody (TNF-alpha blocker)	UCB, Inc.	Crohn's disease, rheumatoid arthritis
Pegloticase	Uricase	Savient	Chronic gout

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Perfluoropolymers in Membranes

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Synonyms

Perfluoropolymers PFP

Perfluoropolymers are fluorocarbon-based polymers with multiple carbon-fluorine bonds. This unique class of polymers has been widely used in membrane technology for their excellent

chemical and thermal stability, high mechanical strength, and versatile processability. The main application areas of fluoropolymer membranes have been focused on microfiltration (MF), ultrafiltration (UF), and battery separators. Recently, however, the application ranges are expanding into new innovative applications like membrane bioreactor (MBR), membrane distillation (MD), membrane crystallization (MCR), and pervaporation.

Since each application calls for different membrane performances, membranes need to be tailored using appropriate materials and fabrication methods. Some of the key fluoropolymers used to prepare membranes are summarized in Table 1.

PVDF is by far the most widely used fluoropolymer to prepare membranes. Although chemically inert (nonreactive), it has high solubility in polar aprotic solvents, allowing PVDF membranes to be fabricated via the nonsolvent-induced phase separation (NIPS) method. PVDF is also a semicrystalline and thermoplastic polymer with a relatively low melting point around 170 °C, allowing it to be melt processed into different morphologies. In addition, with appropriate solvents, highly porous and uniform PVDF membranes can be prepared via the thermally induced phase separation (TIPS) method. As most fluoropolymers are intrinsically hydrophobic (i.e., low surface energy), fluoropolymeric membranes for water treatment applications are typically post-treated using different hydrophilization methods. In addition, depending on the fabrication method and protocol, PVDF can assume different crystal morphologies (α -, β -, and γ -phases) where β -phase can yield antifouling effects.

ECTFE is a semicrystalline copolymer of ethylene and chlorotrifluoroethylene with excellent chemical resistance to corrosion and solvent degradation. Compared to the PVDF polymer, processing ECTFE into membranes is slightly more cumbersome as it does not dissolve in any known solvent at ambient temperature. However, with appropriate solvents at high temperatures (150–250 °C), ECTFE membranes can be fabricated via the TIPS method. The excellent thermal

Perfluoropolymers in Membranes, Table 1 Main perfluoropolymers used to prepare membranes (Cui et al. 2014)

Polymer	Chemical structure
PVDF (e.g., Solef [®] , Kynar [®]) poly(vinylidene fluoride)	$\left[\text{CH}_2 - \text{CF}_2 \right]_n$
ECTFE (e.g., Halar [®]) poly(ethylene chlorotrifluoroethylene)	$\left[\text{CH}_2 - \text{CH}_2 - \underset{\text{Cl}}{\overset{\text{F}}{\text{C}}} - \text{CF}_2 \right]_n$
PTFE (e.g., Teflon [®]) poly(tetrafluoroethylene)	$\left[\text{CF}_2 - \text{CF}_2 \right]_n$
PFSA (e.g., Nafion [®]) perfluorosulfonic acid	$\left[\text{CF}_2 - \text{CF}_2 \right]_m \left[\text{CF}_2 - \underset{\text{O}}{\overset{\text{O}}{\text{CF}}} \right]_n$ $\begin{array}{c} \text{O} \\ \\ \text{CF}_2 \\ \\ \text{F}_3\text{C} - \text{CF} \\ \\ \text{O} - \left[\text{CF}_2 \right]_y \text{SO}_3\text{H} \end{array}$

stability of ECTFE membranes allows them to be applied in niche applications as ECTFE membranes can withstand continuous operation at temperatures higher than 150 °C in harsh chemical conditions. Although ECTFE membranes are at the development stage with no commercial product in the market, it has a strong potential in organic solvent nanofiltration (OSN) and pervaporation applications.

PTFE polymer is well known under the trademark Teflon[®] with remarkable chemical, mechanical, and thermal stability. Although PTFE has many ideal characteristics for membrane applications, fabricating reliable PTFE membranes has been rather challenging. As no known solvent can dissolve this unique polymer, PTFE membranes are typically fabricated using melt-processing techniques, but its high-melt viscosity has been made a key hurdle to overcome. Nevertheless, commercial MF PTFE membranes are widely used in various industries exploiting their chemical and thermal stability.

PFSA polymers contain sulfonyl branches on PTFE backbone, exhibiting proton conductivity

without losing the high mechanical and thermal stability of PTFE. Naturally, PFSA polymers found large markets in fuel cell industries as proton exchange membranes (PEMs). One of the well-known PFSA polymers carries a trademark Nafion[®]. Although many competitors came into the market after the discovery of Nafion[®] in the late 1960s, it still remains to be the best option in the fuel cell technology.

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Perfluoropolymers PFP

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Permeability

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Synonyms

Gas permeability

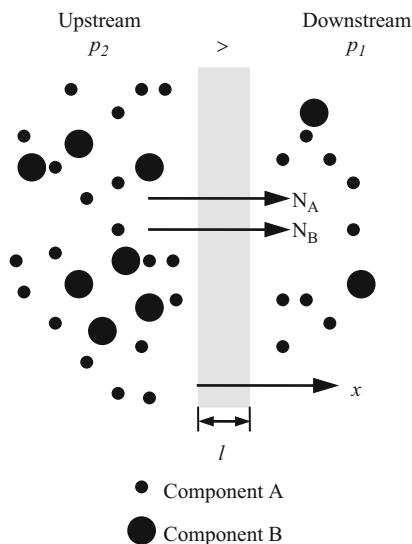
Small molecule transport through a dense or nonporous polymeric film is often described by the solution-diffusion model, which has been applied to various membrane separation processes such as reverse osmosis, pervaporation, and gas separation (Graham 1866; Wijmans and Baker 1995; Paul 2004; Baker 2012). Before the solution-diffusion model became well accepted in the 1970s, the pore flow model was also used. The pore flow model is based on a very direct physics interpretation and now is only used by very few people to interpret the reverse osmosis process (Baker 2012).

Based on the solution-diffusion model, the transport of small molecule in the polymer follows three steps, which is illustrated in Fig. 1 for gas separation (Graham 1866; Wijmans and Baker 1995; Lin and Freeman 2006):

1. Feed gas at a high (i.e., upstream) pressure, p_2 , dissolves into the feed side surface of the film.
2. The dissolved gas molecule diffuses through the film due to a concentration gradient.
3. Finally, the gas molecule desorbs from the permeate side surface at the downstream (i.e., low pressure) face of the film.

In the absence of chemical reaction between the gas and polymer, the diffusion of dissolved penetrant is the rate-limiting step in this process, which can be described using Fick's law (Wijmans and Baker 1995; Baker 2012).

The steady-state permeability of small molecule A, P_A , through a film of thickness l is defined as (Wijmans and Baker 1995):



Permeability, Fig. 1 Transport of gases A and B across a polymeric film (Lin and Freeman 2006), which can be described using the solution-diffusion model

$$P_A \equiv \frac{N_A \cdot l}{A_m \cdot (p_2 - p_1)} \quad (1)$$

where N_A is the steady-state flux of component A through the polymer and A_m is the active area for permeation. Permeability can be calculated by directly measuring the parameters shown in Eq. 1. Permeability coefficients of gas and vapor are commonly expressed in Barrers, where 1 Barrer = 1×10^{-10} cm³(STP) cm/(cm² s cmHg) (Stern 1968).

When the permeate pressure is much less than the feed pressure, gas permeability can be written as: (Wijmans and Baker 1995)

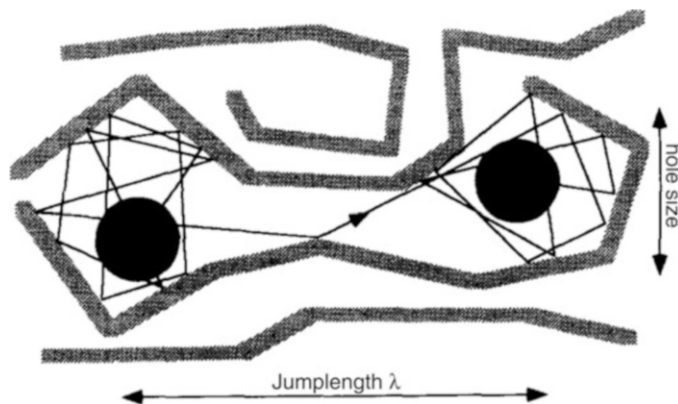
$$P_A = D_A \times S_A \quad (2)$$

where S_A is the apparent sorption coefficient or solubility of penetrant A in the polymer. The gas and vapor permeability can be directly measured using the constant pressure-variable volume or constant volume-variable pressure method (Felder and Huvard 1980; Lin and Freeman 2006).

The permeation of the gas through polymer films can also be modeled using molecular

Permeability,

Fig. 2 Schematic of the CO₂ molecule movement from one confined void to another void in a polyimide via random motion (Smit et al. 1992)



dynamic simulation (Smit et al. 1992; Wang et al. 2006). For example, Fig. 2 shows the schematic of CO₂ diffusion in a polyimide matrix. Polymer chains follow random work, which creates temporary voids and channels. The CO₂ molecules can jump from one void to another void via the random motion.

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Permeability Coefficient

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The transport property of a penetrant through a film is often characterized by the permeability coefficient. The steady-state permeability coefficient of gas A, P_A , through a film of thickness l is defined as: (Wijmans and Baker 1995)

$$P_A \equiv \frac{N_A \cdot l}{p_2 - p_1} \quad (1)$$

where p_2 and p_1 are upstream (i.e., high) and downstream (i.e., low) pressures, respectively. Permeability coefficients are commonly expressed in Barrers, where 1 Barrer = $1 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ s cmHg})$ (Stern 1968).

The one-dimensional flux of gas A through the film in the x direction (i.e., N_A) can be described by the solution-diffusion model and Fick's Law (Bird et al. 2002; Ghosal and Freeman 1994):

$$N_A = -D \frac{dC_A}{dx} + w_A(N_A + N_P) \quad (2)$$

where D is the gas diffusion coefficient in the film, C_A is the local concentration of dissolved gas, and w_A is the weight fraction of gas A in the film. N_P is the flux of the membrane, which is typically taken

to be zero. Consequently, Eq. 2 reduces to (Ghosal and Freeman 1994; Koros et al. 1988):

$$N_A = -\frac{D}{1-w_A} \frac{dC_A}{dx} \quad (3)$$

Combining Eqs. 1 and 3 and integrating from $x = 0$ ($C = C_2$) to $x = l$ ($C = C_1$), one obtains:

$$P_A = D_A \frac{C_2 - C_1}{p_2 - p_1} \quad (4)$$

where D_A is the concentration-averaged effective diffusion coefficient in the range for C_1 to C_2 :

$$\begin{aligned} D_A &= \frac{1}{C_2 - C_1} \int_{C_1}^{C_2} \frac{D}{1-w_A} dC \\ &= \frac{1}{C_2 - C_1} \int_{C_1}^{C_2} D_{eff} dC \end{aligned} \quad (5)$$

where D_{eff} is the local effective diffusion coefficient.

In general, it is challenging to directly measure gas average diffusivity. Instead, gas permeability and gas solubility are often measured independently, and gas diffusivity is inferred from these measurements as described below (Lin and Freeman 2006). For simplicity, experiments are often designed so that $p_1 \ll p_2$ and, consequently, $C_1 \ll C_2$. In this limit, Eq. 4 reduces to (Freeman (1999), Wijmans and Baker (1995)):

$$P_A = D_A \times S_A \quad (6)$$

where $S_A = C_2/p_2$ is the apparent sorption coefficient or solubility of penetrant A in the polymer. Therefore, by measuring gas permeability at an upstream pressure of p_2 and solubility at a pressure of p_2 , one can calculate average gas diffusivity, D_A . Gas selectivity, a measure of the ability of polymers to separate two gases A and B, is expressed (Wijmans and Baker 1995):

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \frac{S_A}{S_B} \quad (7)$$

As indicated in Eq. 5, the diffusion coefficient is an average over the concentration range from 0 to C_2 . The local effective diffusion coefficient, D_{eff} , characterizing penetrant diffusivity in the polymer at a penetrant concentration of C_2 , can be evaluated using an equation obtained by taking the derivative of both sides of Eq. 4 with respect to C (Koros and Fleming 1993; Merkel et al. 2000):

$$D_{eff}(C_2) = \left[P_A + p \frac{dP_A}{dp} \right]_{p_2} \left(\frac{dp}{dC_2} \right)_{p_2} \quad (8)$$

which requires the pressure dependence of permeability and solubility to calculate D_{eff} .

Methods to measure pressure dependence of permeability and solubility have been described (Felder and Huvard 1980; Lin and Freeman 2006). Table 1 shows gas permeability coefficients and selectivity of a few commercial gas separation membrane materials, which are arranged in nitrogen permeability coefficients

Permeability Coefficient, Table 1 Gas permeability coefficients and selectivity of several commercial membrane materials at 35 °C, including cellulose triacetate (Puleo et al. 1989), polysulfone (Aitken et al. 1992), polycarbonate (Stern 1994), polyphenylene oxide (Koros et al. 1988), polydimethylsiloxane (Merkel et al. 2000), and Teflon AF2400 (Arcella et al. 2003; Merkel et al. 2006)

Polymer	Permeability (Barrer)				Selectivity	
	N ₂	O ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄
Cellulose triacetate	0.23	1.46	0.20	6.56	6.3	32.8
Polysulfone	0.25	1.4	0.25	5.6	5.6	22
Matrimid	0.32	2.12	0.28	10.0	6.6	35.3
Polycarbonate	0.33	1.6	0.36	6.8	4.8	19
Polyphenylene oxide	3.81	16.8	4.3	61	4.41	14.2
Polydimethylsiloxane	400	800	1,200	3,800	2.0	3.2
Teflon AF2400	490	990	340	2,800	2.0	8.2

from low to high (Koros et al. 1988; Park and Paul 1997; Pauly 1999; Robeson 1991; Stern 1994). The permeability coefficients can vary dramatically depending on the penetrant physical property and the polymer structure.

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Permeance

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Synonyms

Gas permeance

The permeance is a characteristic of a membrane expressing the ability of a species to penetrate and permeate a membrane of a specific thickness. It is an overall coefficient to be used in the evaluation of the flux of any species permeating the membrane as well membrane selectivity.

The driving force at the basis of mass transport through the membrane, in most of the membrane operations such as reverse osmosis, nanofiltration, ultrafiltration, microfiltration, gas separation, membrane distillation, membrane contactors, etc., is a difference of feed and permeate pressures or species partial pressures. This is valid for both dense membranes used in reverse osmosis and gas separation and porous ones utilized in the other operations. In addition, the permeance most often does not depend on the permeation driving force; thus, the following equation defines the flux of each permeating species (*i*th) as the product of permeance and driving force:

$$\text{Flux}_i = \text{Permeance}_i * \text{driving force}_i$$

The reverse of this equation allows the permeance to be calculated; thus, the membrane permeance is evaluated for each species as the ratio between the own flux and the related driving force.

The driving force is calculated as function of the pressure values in the bulks of the feed and permeate streams or volumes for continuous or batch systems, respectively. This means, the permeance has to take into account all the mass transfer resistance encountered by the molecules along the path followed for their permeation from the bulk of the feed side to the bulk of the permeation side. These resistances are those in the film on the feed side, in the separating membrane layer, in the supporting membrane layer, in the support eventually present, in the film on permeation side, and in the fouling as well.

The units of the permeance depend on the permeation mechanism at the basis of mass transport through the membrane. In most of the membrane operations as those before reported for which the driving force is a difference of feed and permeate pressures, the permeance units are:

$$\begin{aligned} & \text{mol m}^{-2}\text{s}^{-1}\text{Pa}^{-1} \\ & (\text{or m}^3\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}, \text{ or m}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}, \\ & \text{ or L m}^{-2}\text{s}^{-1}\text{Pa}^{-1}, \text{ or etc.}) \end{aligned}$$

However, the driving force of the permeation in inorganic membranes, such as the Pd-based and perovskite ones, is the difference of the square root of the pressures on both membrane sides since the hydrogen (see Sieverts' law) or oxygen molecules permeating these membranes are dissociated in atoms before their permeation in the selective membrane layer. Consequently, the permeance units are:

$$\begin{aligned} & \text{mol m}^{-2}\text{s}^{-1}\text{Pa}^{-0.5} \\ & (\text{or m}^3\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-0.5}, \text{ or m}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}, \\ & \text{ or L m}^{-2}\text{s}^{-1}\text{Pa}^{-0.5}, \text{ or etc.}) \end{aligned}$$

Power different from 0.5 is also utilized for the feed-permeate pressure difference when the diffusion in the separating layer is not the only rate-determining step but surface phenomena are significant.

Examples

The permeance of a reverse osmosis membrane, operating under a feed-permeate pressure difference of 50 bar with a water flux of $60 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$, is $60/50 = 1.2 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$.

The permeance of a gas separation membrane having a CO_2 flux of $5 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ and operating under a feed-permeate partial pressure difference of 10 bar is $500 \text{ dm}^3(\text{STP}) \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (ca. $62 \text{ nmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$).

A Pd-based membrane operating at 5 and 1 bar as feed and permeate hydrogen pressures, respectively, shows a hydrogen flux of $300 \text{ nmol m}^{-2} \text{ s}^{-1}$. Thus, hydrogen permeance is ca. $243 \text{ nmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$.

Permeate

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The permeate is the whole mass permeated of the membrane containing the different species which permeated the membrane itself. On the other membrane side with respect to the feed, it is collected in a volume or as a stream, leaving the membrane module in a batch or continuous operations, respectively.

Together with the retentate, the permeate is one of the two outlets of a membrane unit. The other two streams are the feed and, optionally, the sweep.

Cross-References

- [Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study](#)

Permeate Gap Membrane Distillation (PGMD)

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Permeate gap membrane distillation (PGMD) represents a specific configuration of the membrane distillation (MD) process.

In a MD process, a hydrophobic highly porous membrane separates an aqueous feed solution from the distillate. The hydrophobic membrane property prevents the liquid phase from entering the membrane structure; thus, liquid-vapor interfaces are established on both sides of the membrane. By applying a temperature difference, evaporation takes place on the feed (or evaporator) side; the vapor penetrates the membrane pores and condenses on the permeate (or condenser) side. The separation is based on the phase change; thus, the product quality is usually very high and does not depend on feed concentration or the membrane structural properties. The coupled heat and mass transfer through the membrane includes vapor flux, latent heat of evaporation, and conductive heat transfer.

In conventional direct contact membrane distillation (DCMD) process, the heat of evaporation is supplied by the hot feed stream, and the cooling is maintained by the cold stream, respectively.

In permeate gap membrane distillation (PGMD) process, a third channel is introduced by an additional non-permeable foil, similar to air gap membrane distillation (AGMD). The basic PGMD channel arrangement is given in Fig. 1.

In PGMD, usually this channel is filled with permeate during operation. One significant advantage of this arrangement is the separation of permeate from the cooling fluid. Therefore, the coolant can be any other liquid, such as cold feed.

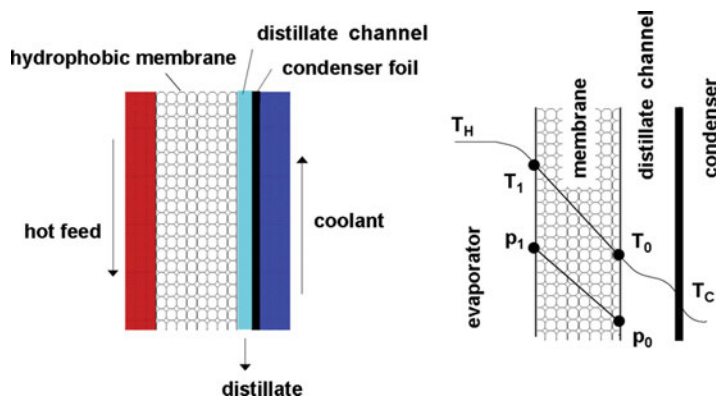
The presence of the permeate gap and the non-permeable foil introduce additional heat transfer resistances, which lead to a reduction of the effective temperature difference across the membrane. This heat transfer resistance is to be minimized, by designing a very thin permeate gap and using thin foils.

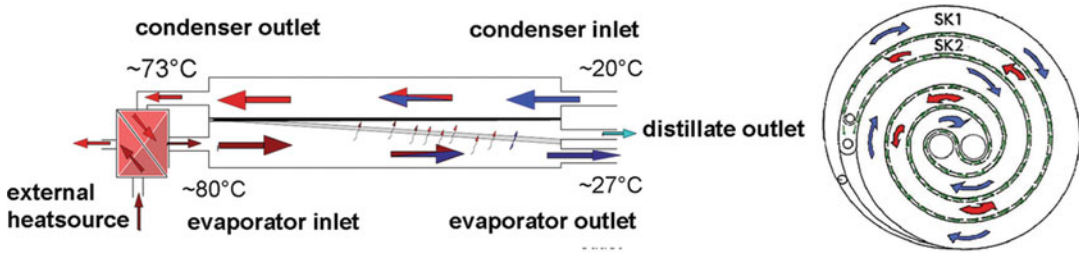
For special applications this concept can even be further developed, e.g., by introducing a second foil at the feed side. Here, the heating function can be decoupled from the feed solution as well (Hausmann et al. 2011).

In module design, the PGMD concept provides the opportunity for internal heat recovery. Modules are usually designed based on plate and frame or spiral wound concepts.

Figure 2 shows the channel arrangement for a PGMD module with integrated heat recovery. The PGMD channel arrangement is transferred into a compact spiral package. Full-scale modules of this type were developed and fabricated at Fraunhofer ISE (Winter et al. 2011). The total

Permeate Gap Membrane Distillation (PGMD), Fig. 1 Basic channel arrangement and temperature profile for PGMD (Winter et al. 2011)





Permeate Gap Membrane Distillation (PGMD), Fig. 2 Principle channel arrangement of a spiral wound PGMD module (Winter et al. 2011)

membrane area is 5–15 m². The module concept goes back to a patent of W. L. Gore from 1985 (Gore et al. 1985).

This type of module is quite suitable to follow the transient behavior of thermal energy input from renewable sources. Thus, an integration to solar thermal collectors or waste heat is easily applicable. Various demonstration plants for desalination using PGMD spiral wound modules have already been tested in the field (Raluy et al. 2012).

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Permeating Flux

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All the species permeating a membrane generate a stream passing through the membrane, a stream characterized by a flow rate according to the actual operating conditions. A permeating flux is defined for this stream as the ratio of the permeating flow rate and the membrane area.

$$\text{Permeating Flux} = \frac{\text{Permeating Flow Rate}}{\text{Membrane Area}}$$

The permeating flux can be defined as well for *i*th species as the ratio of the flow rate of the referred species and the membrane area.

$$\text{Permeating Flux}_i = \frac{\text{Permeating Flow Rate}_i}{\text{Membrane Area}}$$

It is a fraction of the total permeating flux and can be expressed as product of the molar fraction of the *i*th species and the permeating flux of all the species.

$$\text{Permeating Flux}_i = \text{Molar Fraction}_i \cdot \text{Permeating Flux}$$

The permeating flux can be defined for each elementary membrane area element or for the whole membrane area. In the first case, it is a function of the spatial coordinates such as, for instance, the

membrane length. In the latter case, the permeating flux corresponds to the integration of the permeating flow rate on the whole membrane area of the elementary one divided for the whole membrane area.

Permeation Number

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The permeation number expresses (Brunetti et al. 2010), for each species, a comparison (ratio) between two main transport mechanisms involved in a membrane separation unit:

1. The mass transport through the membrane
2. The convective mass transport for feeding the membrane unit

For the i th species, it is given by the equation

$$\text{Permeation Number}_i = \frac{\text{Permeance}_i \text{ Membrane Area} \text{ Feed Pressure}}{\text{Feed Molar Fraction}_i \text{ Feed Flow Rate} \text{ Pressure Ratio}}$$

It is a dimensionless number to be used in sizing the permeation unit. A low value means a low fraction of the referred i th species can pass through the membrane; vice versa, a high value means a large fraction of i will be in the permeate stream.

A value of zero means no membrane separation, that is, permeance equals to zero or equivalently no membrane area available for permeation.

The pressure ratio is the ratio of the feed to the permeate pressures.

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Permeation Reduction Maps

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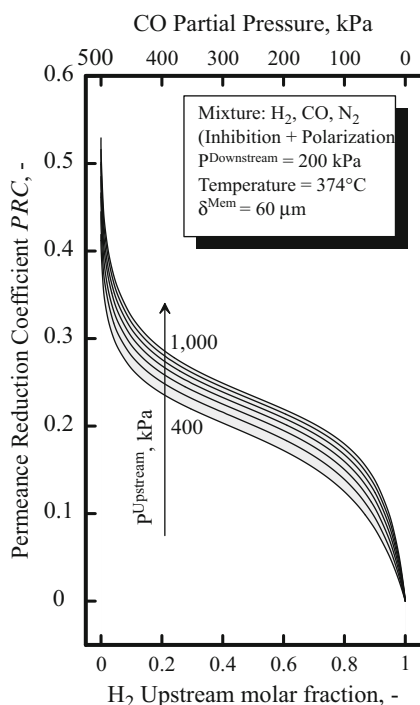
With reference to the definition of the overall permeation reduction coefficient (PRC) – whose definition is briefly recalled in Eq. 1 – the so-called permeation reduction maps refer to diagrams where PRC is plotted as a function of several operating conditions, like hydrogen partial pressure, temperature, total pressure, and membrane geometrical parameters.

$$[\text{Flux}]_i^{\text{Actual}} = (1 - PRC_i) \times [\text{Flux}]_i^{\text{Max}} \quad (1)$$

The usefulness of the permeation reduction maps consists in reading a value of PRC based on the operating conditions of interest and using it directly in Eq. 1 to evaluate the actual flux, i.e., the flux reduced from the maximum one by the effect of the unwanted phenomena, for example, concentration polarization and inhibition.

Permeation reduction maps can be built both by experimental campaigns and by computer simulations of the hydrogen permeation process.

An example of *permeation reduction map* including the effect of concentration polarization and inhibition by CO is shown in Fig. 1 for hydrogen permeation through Pd-based membranes. In this figure, generated by simulation, PRC is depicted as a function of hydrogen molar fraction and CO partial pressure for different values of total upstream (feed) pressure (Caravella et al. 2010).



Permeation Reduction Maps, Fig. 1 Example of permeation reduction map in terms of permeation reduction coefficient as a function of hydrogen molar fraction in the upstream and CO partial pressure for different values of upstream pressure evaluated by computer simulation in the conditions reported in the legend (Adapted from Caravella et al. (2010))

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Permselectivity

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Synonyms

Membrane permselectivity; Rejection

Permselectivity in Dense Membranes

Permselectivity is the most important membrane property to evaluate the quality of membrane separation. The capability of a membrane to separate different components from each other can be expressed by selectivity. Considering a two-component mixture *A* and *B*, the selectivity is given by the ratio of their permeability coefficients as follows (Strathmann et al. 2006):

$$S_{A,B}^p = \frac{P_A}{P_B}$$

Here $S_{A,B}^p$ is the permselectivity of a membrane toward components *A* and *B*, and P_A and P_B are their permeability coefficients. Materials with high permeability and selectivity are desirable. Higher permeability decreases the amount of membrane area required to treat a given compound, thereby selectivity results in higher purity product.

For dense membranes, the permeability coefficient (P) can be expressed by the following equation:

$$P = D \times S$$

where D and S are the diffusivity and the solubility coefficients of the gas species, respectively.

Permselectivity in Porous Membranes

For porous membranes, the hydraulic permeability (L_p) is defined as a volume of permeate passing for the unit time through a unit of membrane surface area under a certain hydrostatic pressure:

$$L_p = \frac{V}{At\Delta P}$$

where V is the permeate volume (L), t is the time (h), and ΔP is the transmembrane pressure (bar). For the processes based on porous membranes, the quality of separation that the membrane provides can be expressed in terms of rejection, which is given by:

$$R_A = 1 - \frac{C_A^{\text{permeate}}}{C_A^{\text{feed}}}$$

Here R_A is the rejection of component A by the membrane and C_A^{permeate} and C_A^{feed} are the concentrations of the component A in the two phases. The value of rejection varies between 0 (no selectivity) and 1 (complete retention of the solute).

Permselectivity in Ion-exchange Membranes

In ion-exchange membranes, the permselectivity describes the degree to which an ion of one charge passes through the membrane, while an ion of the opposite charge is retained. This parameter can be calculated from the transport number (T) of the counter- and co-ions in the membrane and the outside solutions. The permselectivity of ion-exchange membrane (Ψ) is given as follows:

$$\Psi^m = \frac{T_{\text{cou}}^m - T_{\text{co}}}{T_{\text{co}}}$$

The transport numbers (T) are defined by:

$$T_i = \frac{z_i J_i}{\sum_i z_i J_i}$$

Here z is the valence, J is the flux, the subscript i refers to cation or anion, the subscripts cou and co refer to counter- and co-ions, and the subscript m refers to ion-exchange membrane. The permselectivity of the membrane approaches zero when the transport numbers of the ions within the membrane are identical to those in the electrolytic solution.

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Permselectivity of Ion-Exchange Membranes

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The permselectivity of a membrane is determined by the ratio of the flux of specific components to the total mass flux through the membrane under a given driving force. In ion-exchange membranes, the permselectivity is related to the transport of electric charges by the counterions (Strathmann et al. 2006; Tonaka 2015). The permselectivity of an ion-exchange membrane, i.e., its charge selectivity, is determined by the concentrations of counter- and coions in the membrane, which again depends mainly on the ion-exchange capacity of the membrane and the ion concentration in the outside solutions because of the Donnan exclusion as discussed earlier. The permselectivity can be calculated from the transport number of the counter- and coions in the membrane and the outside solutions.

The permselectivity of a membrane is given by:

$$\Psi^m = \frac{T_{\text{cou}}^m - T_{\text{co}}}{T_{\text{co}}} \quad (1)$$

The transport numbers are defined by:

$$T_i = \frac{Z_i J_i}{\sum_i z_i J_i} \quad (2)$$

Here Ψ is the permselectivity, T is the transport number, z is the valence, and J is the flux; the subscript i refers to cation or anion, the subscripts cou and co refer to counter- and coions, and the superscript m refers to the ion-exchange membrane.

In a cation-exchange membrane, the cation is the counterion and the anion the coion, while in an anion-exchange membrane, the anion is the counterion and the cation the coion.

An ideal permselective cation-exchange membrane, for instance, would be permeable for positively charged cations (counterions) only. The permselectivity of a membrane approaches zero when the transport numbers of the ions within the membrane are identical to those in the electrolytic solution.

To determine the membrane permselectivity, respectively, two methods can be applied. The first method is based on a measurement of the increase in concentration of certain ions in the concentrate and the decrease in the dilute solution during electrodialysis of a test solution and by measuring the amount of current passing through the unit. From the current utilization, the permselectivity of the membrane can be calculated. With this “dynamic” measurement, water transport due to electroosmosis and osmosis is taken into account, and the “true” membrane permselectivity is obtained. The dynamic method, however, is rather time-consuming and affected by concentration polarization at the membrane surfaces.

A faster “static” method for the determination of membrane permselectivities, which is not affected by boundary layer transport phenomena, is based on the measurement of the potential gradient across a membrane which separates two electrolyte solutions of different concentrations. The static method, however, does not take the water transport through the membrane into account and is referred to as “apparent” permselectivity.

The potential between two electrolyte solutions of different concentrations, i.e., the membrane potential, consists of the two Donnan potentials between the membrane and the adjacent solutions and the diffusion potential across the membrane.

$$\varphi_m = \varphi_{\text{dif}} + \varphi_{\text{Don}}^1 - \varphi_{\text{Don}}^2 \quad (3)$$

Here φ is the potential; the subscripts m , dif, and Don refer to membrane, diffusion, and Donnan potential; and the superscripts 1 and 2 refer to the different solutions.

For a completely permselective membrane, the diffusion potential is zero. The membrane potential is then given by the difference in the two Donnan potentials. For a not strictly permselective membrane, the diffusion potential must be added to the Donnan potential difference to determine the membrane potential. For a single, monovalent salt such as KCl as an electrolyte, the membrane potential between two solutions of the same electrolyte but different concentration can be derived from the general flux equation with the boundary conditions of $\Delta P = 0$ and $I = 0$. By introducing several approximations, such as negligible osmotic flow between the two solutions, constant ion mobility, small concentration gradients across the membrane phase, etc., the potential difference between solutions can be expressed by:

$$\begin{aligned} \varphi_m &= (T_{\text{cou}}^m - T_{\text{co}}^m) \frac{RT}{F} \ln \frac{a_s^1}{a_s^2} \\ &= (2T_{\text{cou}}^m - 1) \frac{RT}{F} \ln \frac{a_s^1}{a_s^2} \end{aligned} \quad (4)$$

For a strictly permselective membrane, the transport number of the counterion is 1, i.e., there is no salt diffusion through the membrane, and the membrane potential is given by:

$$\varphi_{m,\text{sp}} = \frac{RT}{F} \ln \frac{a_s^1}{a_s^2} \quad (5)$$

Here φ_m and $\varphi_{m,\text{sp}}$ are the membrane potentials of a real and a strictly permselective ion-exchange membrane, T_{cou}^m and T_{co}^m are the transport numbers of the counter- and coions in the membrane, a_s is the activity of the salt solution, R is the gas constant, T is the temperature, F is the Faraday constant, and the superscripts 1 and 2 refer to the two solutions separated by the membrane.

The counterion transport number in a not strictly permselective membrane is obtained as follows:

$$\frac{\varphi_m}{\varphi_{m,sp}} = 2T_{\text{cou}}^m - 1 \quad (6)$$

and

$$T_{\text{cou}}^m = \frac{\frac{\varphi_m}{\varphi_{m,sp}} + 1}{2} \quad (7)$$

Introducing Eq. 7 into Eq. 1 and rearranging give the permselectivity of a cation-exchange membrane as a function of the membrane potential:

$$\Psi^m = \frac{\frac{\varphi_m}{\varphi_{m,sp}} + 1 - 2T_{\text{cou}}}{2T_{\text{co}}} \quad (8)$$

Here Ψ^m is the apparent permselectivity of an ion-exchange membrane.

For a salt such as KCl, the transport numbers of cation and anion in the solution are nearly identical, i.e., $T_{\text{cou}} \cong T_{\text{co}} \cong 0.5$, and the permselectivity can be expressed to a first approximation by:

$$\Psi^{\text{cm}} \cong \frac{\varphi_{m,\text{real}}}{\varphi_{m,sp}} \quad (9)$$

Permselectivity of Ion-Exchange Membranes,

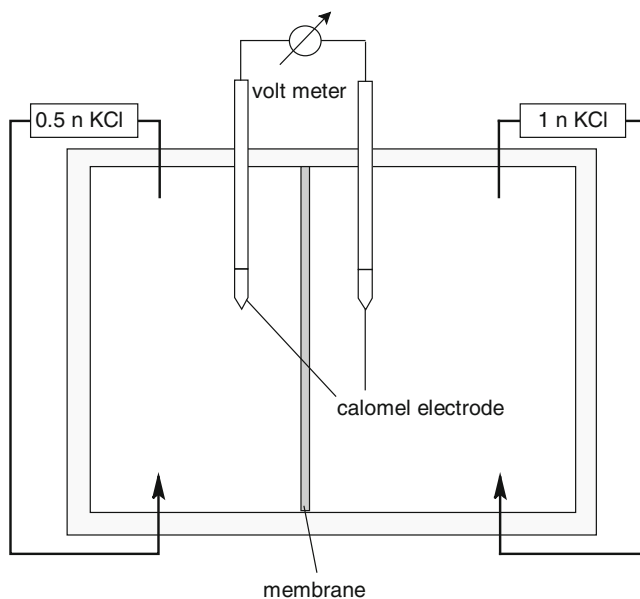
Fig. 1 Schematic drawing illustrating the test cell for determining the membrane potential

The membrane potential is measured with reference electrodes in a test cell consisting of two chambers separated by a membrane as illustrated in Fig. 1.

Both chambers are filled with the same electrolyte solution, e.g., KCl, but with different concentrations, i.e., 0.5 and 1 mol L⁻¹. To avoid a concentration change due to diffusion, the two solutions are well mixed. Then the membrane potential is measured and divided by the potential of a strictly permselective membrane.

Membrane Permeation Selectivity for Different Counterions

The permeation of counter- and coions in ion-exchange membranes is generally quite different, and the counterion permselectivity is close to 1. It is determined mainly by the Donnan exclusion of the coions. However, certain ion-exchange membranes also show permeation selectivity for different counterions. This selectivity is determined mainly by the mobility of the different ions in the membrane, i.e., by the ion size and the structure of the membrane.



The permeation selectivity of different counterions is determined by measuring the fluxes of counterions in a mixture of electrolytes having different counterions but identical coions with reversible electrodes or in a conventional electro-dialysis test. The permeation selectivity of a membrane for different counterions is given by the ratio of their fluxes through the membrane which is identical to the ratio of their transport numbers in the membrane.

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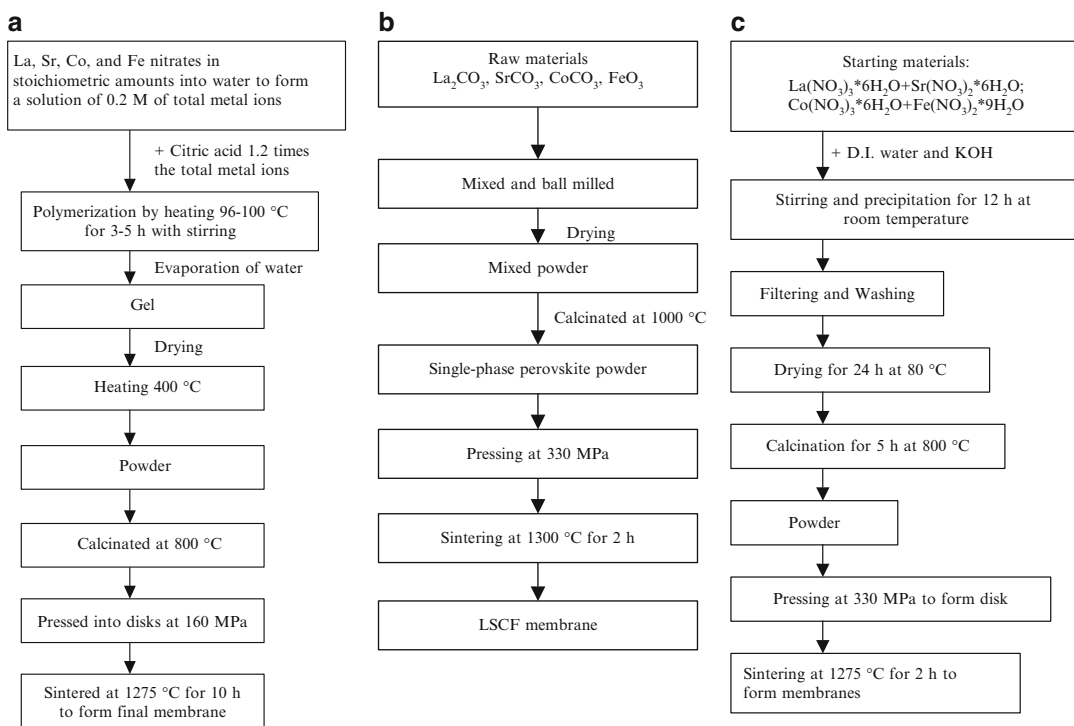
Perovskite Membranes

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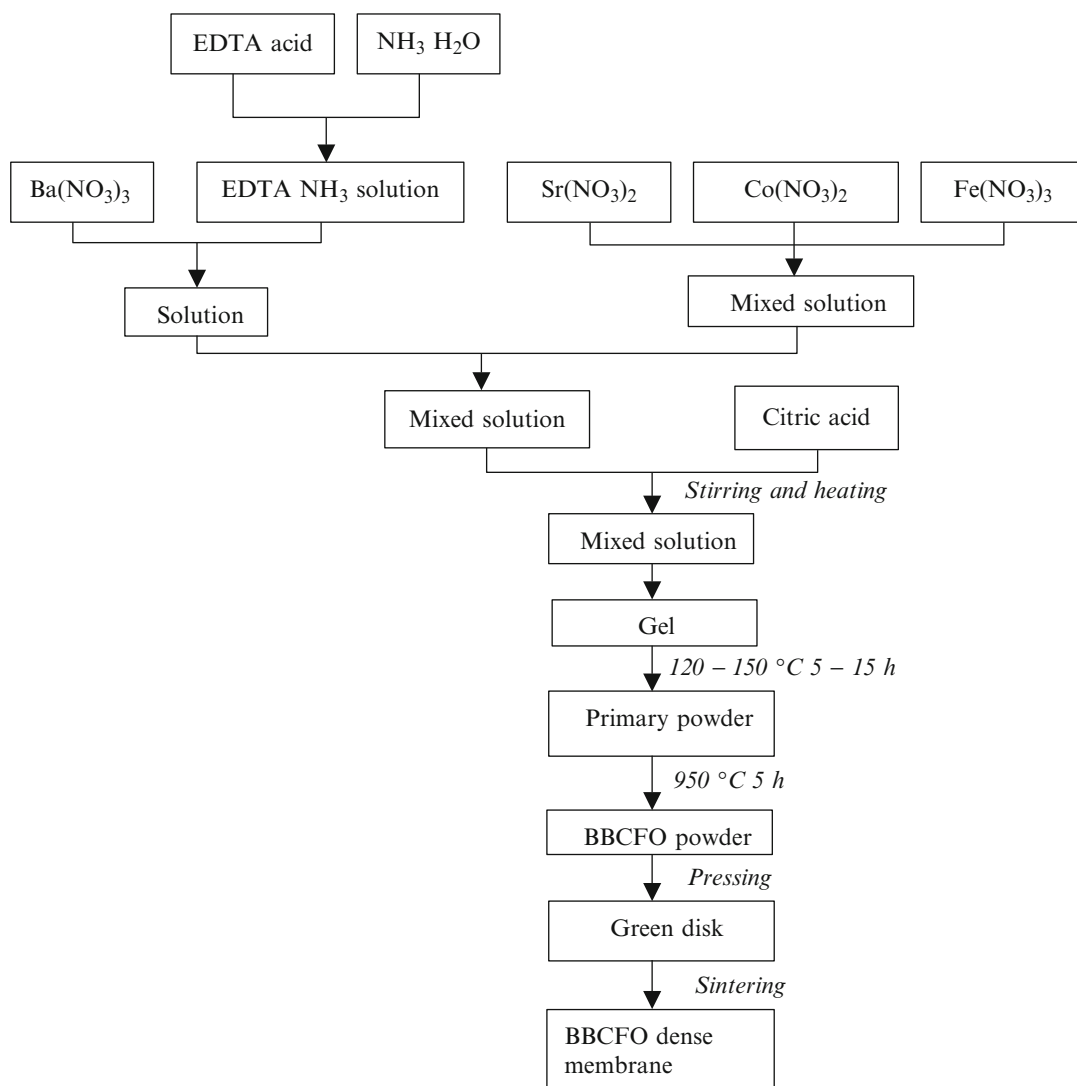
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Perovskite-type membranes have good electron conductivity and oxygen permeability. They have potential applications for oxygen separation from air or oxygen-containing gas mixtures as well as membrane reactors for partial oxidative reactions. Due to mixed-oxygen ion-electron conducting properties, ceramic membranes made of such materials are permeable to oxygen at



Perovskite Membranes, Fig. 1 Membrane perovskite preparation methods: (a) Citrate method; (b) Solid-state method; (c) Coprecipitation method



Perovskite Membranes, Fig. 2 Preparation of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCFO) membrane

elevated temperature without the need for outside electrical circuitry for electron transportation, which is necessary in traditional oxygen pumps.

The traditional methods to synthesize perovskite powder are citrate, solid-state, and coprecipitation method (Qi et al. 2000). They are illustrated in Fig. 1a–c.

A recent method to prepare perovskite $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCFO) powders has

been developed by Shao et al. (2000a, b) as illustrated in Fig. 2. The prepared powder is then pressed into disks in stainless steel molds under hydraulic pressure. The disks are then sintered in a SiC muffle oven at a temperature between 1040 °C and 1500 °C for 2–5 h with a heating and cooling rate of 1 °C min⁻¹ and 2 °C min⁻¹, respectively. Wang et al. (2002) reported about the possibility to obtain also tubular membranes by

extrusion method. The ceramic powder is first mixed with additives (solvents, dispersant, plasticizer, etc.) to improve fluidity of the slip mixture. Then, the slip is extruded through a die at a high pressure to produce the tube-shape membrane. Finally, to remove the organic additives, the membrane is heated at 5 °C/h in the temperature range of 100–450 °C.

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Perovskite Powder Preparation Methods

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Synonyms

Conventional ball milling and calcination; Hydrothermal synthesis; Pertraction coprecipitation and calcination; Spray-pyrolysis

Powders used to manufacture thin films by mainstream methods (e.g., spray coating or screen printing) require properties such as high purity, small particle size, and good sinterability. Therefore, liquid-based methods including spray pyrolysis, hydrothermal synthesis, and coprecipitation

are preferred over low-cost methods (i.e., solid-state synthesis).

Spray pyrolysis is a solution-based method in which elements are dissolved and stabilized in stoichiometric ratios. The solution is fed through a nozzle into a furnace, typically operated at 600–1,000 °C. The liquid evaporates, leaving hollow spheres of metal oxides and organic residues which are collected in a cyclone. Parameters like temperature, concentration, amount of stabilizing agents, and time of flight of the particles influence particle size and the degree of phase purity of the resulting powders. The particles of the resulting powders are agglomerates, usually 1–100 µm in diameter, consisting of small crystallites in the range of 10–100 nm. In most cases, further heat treatments are needed to obtain the desired phase and milling to break up the agglomerates.

Coprecipitation is another solution-based powder synthesis route. Precipitation in its simplest form involves a precursor (e.g., metal salt or alkoxide) containing the desired element which is dissolved in a liquid and brought over the saturation threshold, leading to a supersaturated solution where the solute start to precipitate (hydrolysis). Usually, initial nucleation is induced by either evaporation indirectly increasing the concentration or adding a chemical reagent. Concentration, pH, chemical composition, additives, and temperature are factors which control both nucleation and particle growth. When a sufficient number of nuclei have been formed, the concentration decreases to below the saturation threshold, and the particles start to grow. To produce uniform particles, one desire to have rapid nucleation and slow particle growth. When several elements are precipitated simultaneously, it is often referred to as coprecipitation. In this case, the elements start to precipitate under different conditions, and it is often challenging to find optimal conditions to avoid a mixture of different phases, although further heat treatments are necessary in most cases.

Hydrothermal synthesis is similar to coprecipitation, where nucleation and grain growth are reached through elevated temperature and pressure. The solution is placed inside an

autoclave lined with a plastic coating to avoid corrosion and reactions with the side walls and heated to 100–375 °C which typically leads to pressures up to 20 MPa. The particles are very small, typically 10–20 nm, narrow size distribution and high phase purity, and a range of crystal shapes can be grown. However, drying of the powders after synthesis can lead to hard agglomerates which deteriorate the sintering properties. Upscaling of hydrothermal synthesis to industrial production is a challenge when large amounts are sought.

Calcination is often required after synthesis since most as-prepared powders are multiphase materials consisting of oxides, nitrates, carbonates, and/or other organic species; thus, the powders are heat treated to form a single-phase perovskite. During the calcination step, nitrates and carbonates decompose into oxides, and the cations diffuse within the material forming homogeneous oxide particles. Depending on the material system, controlled atmospheres (i.e., pO_2 , pH_2O) are sometimes necessary to obtain the desired phase by manipulating the oxidation state of the elements and the water (or proton) uptake in the structure. In most cases, the temperature during calcination aims to be as low as possible to prevent particle coarsening which again hinders sintering in later steps of membrane processing.

By milling, agglomerates formed during synthesis can be disintegrated into smaller particles. The most commonly used method today is wet ball milling, in which powders are mixed with a liquid and grinding media in a rotating container. The liquid is often water, ethanol, isopropanol, or acetone, depending on the elements of the perovskite to prevent dissolving the material. The grinding media consist of balls or cylinders made of hard ceramic materials such as yttrium-doped zirconia, alumina, or silicon nitride. After milling, the slurry is dried and powder sieved to the desired particle size distribution. Subsequently, a short thermal treatment is often necessary to burn off organic residuals added during milling, and one should be aware that the powder may be subject to some contaminants from the grinding media. Other methods to break up agglomerates include jet, attrition, and vibrator milling.

Persistent Organic Pollutant

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Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes (Ritter et al. 2007). Because of this, they have been observed to persist in the environment, to be capable of long-range transport, to bioaccumulate in human and animal tissue, to bioaccumulate throughout food chains, and to produce potential human health risks and ecological disturbances.

Many pollutants have been classified as POPs; most of them are halogenated organics and aromatic and aliphatic hydrocarbons. In the field of water treatment, main POPs found in aquatic environments are pesticides, toxins, plastifiers, or pharmaceuticals and personal care products (PPCPs).

Various impacts from different POPs have been identified, the most eye catching being the endocrine-disrupting compounds (EDCs) which can apparently cause fish to change gender. Other POP health impacts have been identified to the reproductive system, the central nervous system, or the immune system (Damstra 2002).

Current studies aimed at controlling and decreasing POP release into the environment (El-Shahawi et al. 2010). However, proper removal techniques of POPs from the environment are still unclear, and different mechanisms could explain the release of POPs into the nature: biosorption on sludge and persistence in the dissolved phase or volatilization. Indeed, for certain volatile POPs like BTEX (benzene, toluene, ethylbenzene, and xylene) or low molecular mass PAH (polyaromatic hydrocarbon), bioavailability could be reduced by volatilization during aerated period in an activated sludge bioreactor (Mozo et al. 2012). Moreover chlorination of remaining compounds in final effluent can form chlorinated

derivatives that are suspected of being carcinogenic to humans (chlorinated hydrocarbons). The acute and long-term toxicity effects of chlorinated compounds on aquatic life have been well documented and have been identified as a major environmental and health issue.

While incurring an impact even at exceedingly low concentrations (tens of nanograms per liter), POPs appear to be well removed by advanced wastewater treatment processes such as activated carbon adsorption, membrane bioreactors (MBRs), nanofiltration and reverse osmosis, and advanced oxidation process (AOP) (Joss et al. 2005).

Because of the increased solid retention time and concentration, MBRs provide more intensive bio-treatment than a conventional activated sludge process, leading to better POP removal efficiency (Hai et al. 2014).

AOP process efficiency on POPs has to be well designed due to the fear that more toxic by-products may result from incomplete oxidation techniques (ozonation, Fenton process). Furthermore, total treatment costs for achieving complete removal of POPs and carbon footprint associated with it could limit the development of such advanced treatment process (James et al. 2014).

Current efforts are more focused on banning the use and production of POPs worldwide rather than removal of POPs.

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Pertraction

► Alcohol Removal by Membrane Operations

Pertraction Coprecipitation and Calcination

► Perovskite Powder Preparation Methods

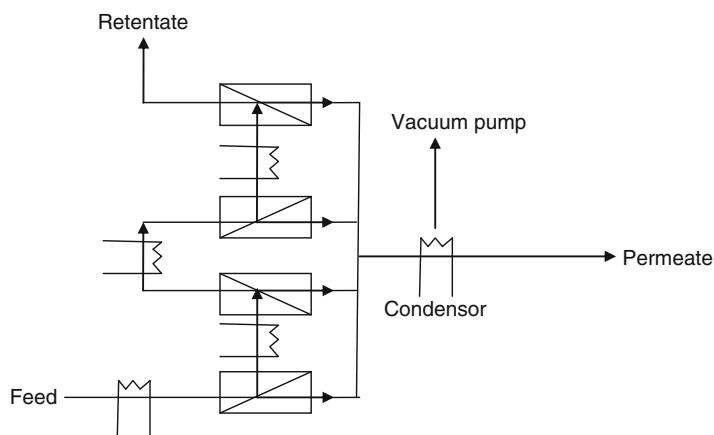
Pervaporation (PV)

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Pervaporation is a membrane separation process, in which components from a liquid mixture are selectively transported through a dense or microporous membrane. Pervaporation was mentioned for the first time in 1917 by Kober in a publication reporting on the selective permeation of water from aqueous solutions of albumin and toluene through cellulose nitrate films. "Pervaporation" is a contraction of "permselective evaporation." The permselectivity originates from the membrane itself, which selectively transports components from the feed mixture, due to differences in (mainly) hydrophilicity and molar size.

Pervaporation (PV),
Fig. 1 Pervaporation
 modules in series with
 intermediate heat
 exchangers



Evaporation is obtained by a low partial pressure at the permeate side of the membrane, either by using a vacuum or a sweep gas stream. The heat of vaporization of the permeating components has been supplied to the feed. In an industrial setup, this heat is supplied by intermediate heat exchangers installed between a number of pervaporation modules in series. This is shown in the figure below (Fig. 1).

Permeation through the membrane in pervaporation can be described in two different ways. The first is the use of pore flow model (and derived models), developed by Okada and Matsuura (1991). The basic assumption of such models is that the membrane is considered to be a bundle of straight, cylindrical pores distributed across the surface layer of the membrane. Transport (and thus, separation) is achieved by liquid permeation followed by vapor permeation through nanometer-scale pores, due to a pressure difference over the membrane. Convective transport is assumed within the pores with an intermediate phase change due to the vacuum at the permeate side or the use of a sweep gas (Shieh and Huang 1998a, b; Lipnizki and Trägårdh 2001). The second approach is the solution-diffusion model, developed by Graham and introduced to pervaporation by Binning et al. (1961). In this model, the membrane is considered to be nonporous so that transport occurs only by diffusion and not by convection. Transport of a component from the feed solution through the membrane occurs by (1) sorption onto the

membrane, (2) diffusion through the membrane, and (3) desorption from the membrane. The driving force is a difference in chemical potential (due to a partial pressure or activity difference) between feed and permeate side (Lipnizki and Trägårdh 2001).

Three types of separations should be distinguished for pervaporation. In hydrophilic pervaporation, small fractions of water (typical range 1–10 %) are removed from organic solvents, using hydrophilic polymers (typically polyvinyl alcohol (PVA), but also other polymers can be used) or ceramic membranes. Hydrophobic pervaporation makes use of polymeric membranes (hydrophobic, such as polydimethylsiloxane or PDMS) with preferential transport of nonpolar solvents, which can be used to remove organics from an aqueous matrix. The third type of applications is organic-organic separations, which require special membranes allowing to distinguish between different organic solvents; an example is PTMSP (Claes et al. 2011). The most important industrial application is the dehydration of alcohols, although research efforts also indicate a great potential in the water and wastewater treatment sector, in the food and biotechnology industry, and in the chemical industry.

With regard to large-scale industrial application, the earliest mention of an operating pilot plant dates back to 1982 as a demonstration unit for alcohol dehydration was designed to produce 1,200 l per day of 99.2 wt.% ethanol.

This unit clearly demonstrated the low energy consumption of pervaporation compared with that of conventional dehydration of ternary azeotropic distillation after addition of benzene (Feng and Huang 1997; Kujawski 2000; Jonquière et al. 2002).

A membrane separation process closely related to pervaporation is vapor permeation. The only difference concerns the feed, which is a mixture of vapors or vapors and gases in vapor permeation, in contrast to the liquid feed in pervaporation.

Cross-References

- ▶ [Alcohol Removal by Membrane Operations](#)
- ▶ [Dense Membranes](#)
- ▶ [Solution-Diffusion Mechanism](#)
- ▶ [Vapor Permeation](#)

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Pervaporation for Chloroform Separation

Tadashi Uragami

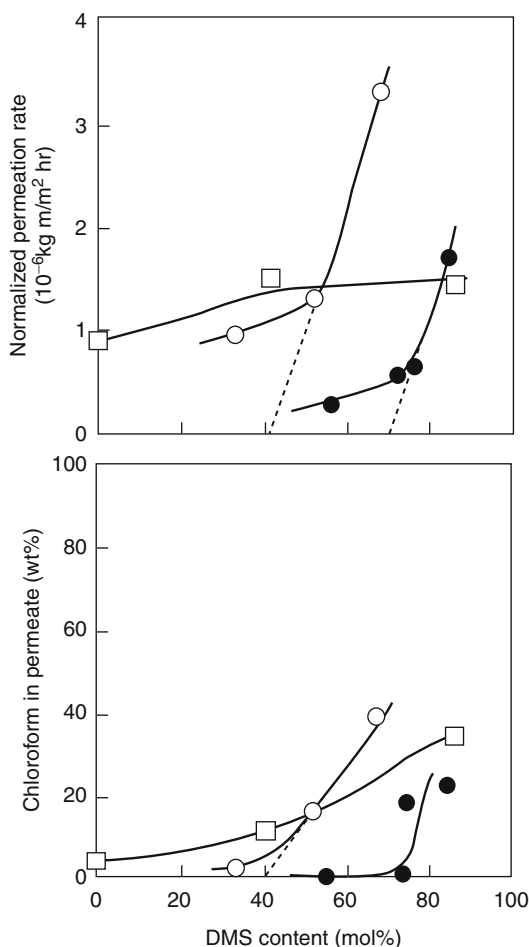
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Chloroform/water-selective membranes are effective for the removal of chloroform in water. These membranes can be contributed to the environmental problem.

Removal of chloroform in an aqueous chloroform solution through the poly(methylmethacrylate)-poly(dimethylsiloxane) (PMMA-g-PDMS), poly(ethylmethacrylate)-PDMS (PEMA-g-PDMS), and poly(*n*-butylmethacrylate)-PDMS (PBMA-g-PDMS) graft copolymer membranes was investigated by pervaporation (PV).

Figure 1 shows the results of PV for an aqueous solution of 0.02 wt.% chloroform through the graft copolymer membranes. The chloroform permselectivity of PMMA-g-PDMS and PEMA-g-PDMS membranes increased dramatically at a DMS content of more than about 40 and 70 mol%, respectively. It is noticeable that the benzene and chloroform permselectivity and the normalized permeation rates for the graft copolymer membranes changed remarkably at the same DMS content. These results suggest that the PMMA-g-PDMS and PEMA-g-PDMS membrane structure changed at the corresponding DMS content. On the other hand, the PBMA-g-PDMS membrane showed a gradual increase in chloroform permselectivity and normalized permeation rate with increasing DMS content. From the above results, it was found that the structural change in the PBMA-g-PDMS membrane with variations in DMS content was quite different from that of the PMMA-g-PDMS and PEMA-g-PDMS membranes (Uragami et al. 2001).

The permeation and separation characteristics of chloroform from water by PV through cross-linked PDMS membranes prepared from



Pervaporation for Chloroform Separation, Fig. 1 Effect of the DMS content on the chloroform concentration in the permeate and normalized permeation rate for an aqueous solution of 0.02 wt.% chloroform through the PMMA-g-PDMS (○), PEMA-g-PDMS (●), and PBMA-g-PDMS (□) membranes by pervaporation

PDMSDMMMA and divinyl compounds, such as EGDM, DVB, DVS, and DVF, were studied (Ohshima et al. 2005). Those membranes showed high chloroform selectivity and permeability. Both chloroform/water selectivity and permeability were affected significantly by the divinyl compound. Furthermore cross-linked PDMSDMMMA membranes showed the highest chloroform/water selectivity. The chloroform/water selectivity was mainly governed by the solubility rather than the diffusion selectivity. With increasing downstream pressure, the chloroform/water selectivity of all cross-linked PDMSDMMMA membranes increased, but the permeability decreased. A -PDMSDMMMA-DVF membrane exhibited a normalized permeation rate of $1.9 \times 10^{-5} \text{ kgm (m}^2\text{h)}^{-1}$ and a separation factor for chloroform/water of 4,850, yielding a separation index of 9,110.

PV experiments were carried out using poly(vinylidene fluoride) (PVF₂) flat-sheet membranes with different thickness for chloroform/water mixtures (Khayet and Matsuura 2004). In Table 1 the permeation rates for chloroform and water and the separation factor, $\alpha_{\text{CH}_3\text{Cl}/\text{H}_2\text{O}}$, are listed. With increasing membrane thickness, the separation factor for the chloroform/water increased, and the permeation rates for water and chloroform decreased. In fact, the selectivity of the PVF₂ membranes is associated not only with the surface characteristics but also with the diffusion through the membrane bulk structure.

Pervaporation for Chloroform Separation, Table 1 Permeation separation characteristics for chloroform/water mixture during PV (Khayet and Matsuura 2004)

Membrane thickness (μm)	Permeation rate for water ($10^{-4} \text{ kgm}^{-2} \text{ s}^{-1}$)	Permeation rate for chloroform ($10^{-5} \text{ kgm}^{-2} \text{ s}^{-1}$)	Separation factor $\alpha_{\text{CH}_3\text{Cl}/\text{H}_2\text{O}}$
38.81	1.69	2.47	146.02
49.77	1.28	1.81	141.69
59.70	1.17	1.91	163.15
83.15	0.87	1.40	160.47
110.77	0.66	1.14	173.32

Initial chloroform concentration 1 kg/m^3 , feed temperature 25°C , reduced pressure $1,666.5 \text{ Pa}$

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Pervaporation Hybrid System

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Synonyms

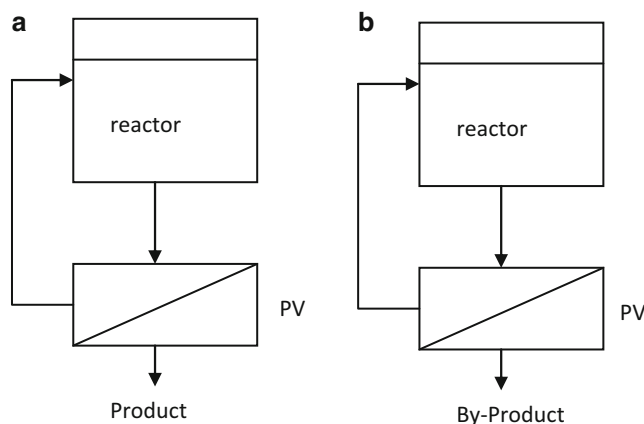
Pervaporation-based hybrid system

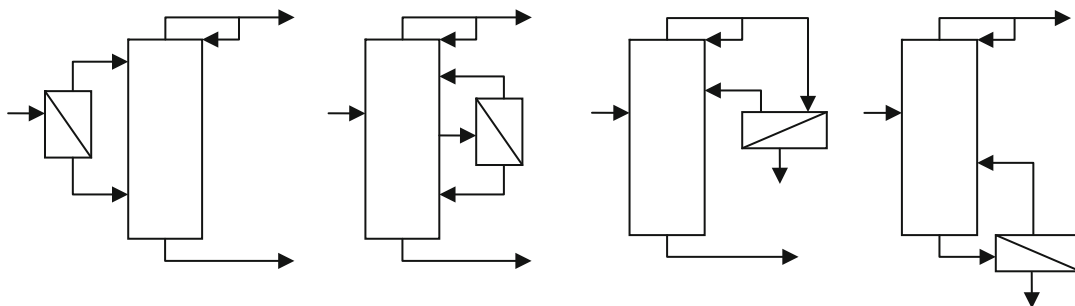
A hybrid system based on pervaporation refers to an integrated entity comprising a pervaporation unit for separation and a second unit in which either a reaction is carried out or a separation with a different method than pervaporation. The

integration by recycling one stream from the pervaporation unit and another stream from the second unit to the pervaporation unit is an essential aspect of the hybridization (without a recycle stream, the system would rather be a separation-separation or reaction-separation sequence) (Van der Bruggen 2010). A hybrid system should have a performance superior to the performance of the sum of the individual processes, which should not be able to carry out the overall process as a stand-alone system (although this is usually understood in the sense that none of the individual processes is able to carry out the overall process *in an economical way*).

Lipnizki et al. (1999) categorize pervaporation hybrid systems into two types, i.e., separation-type and reaction-type hybrid processes. The latter are denoted as R-type hybrid systems; the pervaporation unit can remove either the desired reaction product from the reactor or from a recycle loop (R1-type hybrid system) or a side product (R2-type hybrid system), which is often water. This is shown in Fig. 1 (Lipnizki et al. 1999). R-type hybrid systems with a pervaporation unit for separation are also referred to as pervaporation membrane reactors. R1-type hybrid systems are typical (but not exclusive) for bioconversions, in which the conversion can be enhanced by removal of the conversion product. For example, in the production of bioethanol, the product ethanol acts as an inhibitor for bacterial activity when the concentration becomes too high. Removal of ethanol allows for continuous biological activity,

Pervaporation Hybrid System, Fig. 1 R-type (reaction) hybrid processes: (a) type R1 (removal of reactor product) and (b) type R2 (removal of by-product) (Lipnizki et al. 1999)





Pervaporation Hybrid System, Fig. 2 Integration of pervaporation and distillation in different hybrid configurations

which enhances the yield of ethanol significantly. R2-type pervaporation hybrid systems are typical for equilibrium reactions, in which the yield is enhanced by the removal of a by-product of the reaction. According to the principle of Le Châtelier-Braun, the reaction equilibrium would then shift toward a higher conversion; the net result is that the yield of the desired product is substantially higher, allowing even for full conversion. The most studied examples are esterification reactions, in which an ester is produced from the reaction of an acid with an alcohol. The side product in these reactions is water, which can be easily removed from the reaction medium by a hydrophilic pervaporation membrane. Esterification reactions are often carried out with acetic acid (Van der Bruggen 2010). Pervaporation-assisted esterification of ethanol and acetic acid is often studied, but many other reactions are similar. The principle was patented in 1995 (Datta and Tsai 1995) for the esterification of lactic acid, propionic acid, butyric acid, acetic acid, and succinic acid (and combinations thereof) with an alcohol, including the reaction of acetic acid and ethanol, aided by the use of a pervaporation membrane.

The separation-type hybrid systems based on pervaporation typically combine pervaporation with distillation. Both processes can in principle be used for the same kind of separations, but the separation mechanisms are totally different (based on a difference in volatility for distillation and on a difference in membrane affinity for pervaporation), so that a combination is logical to overcome difficult points in the individual processes. Different configurations based on

integration of pervaporation with a distillation column are shown in Fig. 2 (Van der Bruggen 2010).

The most common difficulties in separations are azeotropic points in distillation, which require complex and energy-intensive solutions when using distillation alone, but are easy in a hybrid setup in which pervaporation is used to overcome the azeotrope. A typical example is the production of ethanol from ethanol-water mixtures. The azeotrope at a concentration of ethanol of ca. 96 % can be overcome by distilling to, e.g., 90 % and continuing with pervaporation for purification of the distillate (and recycling the water-richer retentate back to the distillation column). Various hybrid pervaporation systems can be developed, with a (smaller) distillation column for the final ethanol purification, or a second, more selective pervaporation membrane separation.

Cross-References

- [Pervaporation \(PV\)](#)
- [Pervaporation Membrane Reactor](#)

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Pervaporation in Natural Aroma Processing

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Natural aromas are extremely volatile organic compounds. The aromatic fraction reveals information on the quality of the food and it is directly related to its odor, texture, and taste. Aroma compounds are generally present in very low concentrations (1–20 ppm) even if the complex of the single aromatic compounds in a fruit is very high. Studies of different types of fruits, in fact, indicate that more than 6,000 compounds are responsible of their aroma (Aroujalian and Raisi 2007) belonging to different chemical classes such as alcohols, ketones, aldehydes, esters, carboxylic acids, and phenols. Aroma recovery for food and cosmetic industries continues to be a great challenge for economic and quality reasons (Sampranpiboon et al. 2000). In the fruit juice industry, for instance, where a concentration step is needed, a loss and a degradation of aroma compounds, due to the thermal treatment, can occur. For this reason, in order to restore the original flavor quality of the final product, it is necessary to recover and add these aromatic compounds back to the concentrated juice (Pereira et al. 2006). In this context, pervaporation (PV) is a novel method that can be applied for aroma recovery from diluted aqueous solutions. Pervaporation, in fact, is based on the chemical-physical interaction between membrane material and the components present in the feed. Hydrophobic pervaporation, in particular, is applied to aroma recovery by using hydrophobic membrane materials such as polydimethylsiloxane (PDMS) and polyoctylmethyl siloxane (POMS) (Lipnizki et al. 2002). Compared to other traditional techniques, such as distillation, adsorption, air stripping, and solvent extraction, pervaporation offers numerous advantages: high selectivity, low energy requirement, no chemical addition, and

low-operating temperature. Pervaporation performances are evaluated by taking in consideration the permeate flux and selectivity. Up to now most studies focused on the separation of model binary or multicomponent solutions and just a few of them were based on real feed obtained from fresh fruits (Figoli et al. 2010). Aromas have been isolated by pervaporation from several fruits such as pineapples, grapes, kiwis, strawberries, oranges, and pomegranates. During the last few years, most of the research on aroma recovery has been carried out on laboratory scale. Pervaporation scale-up, in fact, is still underdeveloped due to several limitations mainly due to the membranes and modules, which are not sufficient selective and economic.

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Pervaporation Membrane

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A membrane for pervaporation is a microporous or dense membrane, which selectively transports

components from a liquid mixture due to differences in sorption in the membrane matrix and in diffusion through the membrane to the permeate side. Dense membranes have in principle no pores, whereas microporous membranes have pores in the order of magnitude of 1 nm. The difference, however, is small since the free volume in dense membranes can yield pathways with sizes in the same range as microporous channels.

In general, three types of membranes can be distinguished: (1) hydrophilic membranes, which preferentially transport polar solvents, in particular water, (2) hydrophobic membranes, which preferentially transport nonpolar solvents, and

(3) organophilic membranes, which allow separation of one solvent from another. The separation is based on properties of the membrane material, dominated by polarity interactions but extending to size effects in nanoscale channels.

An overview of hydrophilic membrane materials for pervaporation is given in Table 1. Hydrophilic membranes have a water contact angle below 90° and are either made of polymeric or ceramic materials. They are successfully used for dehydration of solvents. Polymers are often based on polyvinyl alcohol (PVA) or polyimide (PI). Ceramic membranes can be made of silica or zirconia. Zeolites are also used;

Pervaporation Membrane, Table 1 Hydrophilic pervaporation membranes and their applications

Application	Membrane type	Membrane	Reference	Specific target
Dehydration of organic solvents	Polymeric	Polyvinylalcohol (PVA)	Kujawski 2000; Van Baelen et al. 2004; Huang and Jarvis 1970	Methanol, ethanol, n-propanol, IPA dehydration
		Polyimide (PI)	Kim et al. 2000	Ethanol dewatering
		Cellulose and derivatives	Huang and Jarvis 1970	Methanol, ethanol, n-propanol, IPA dewatering
		Sodium alginate	Uragami and Saito 1989; Mochizuki et al. 1990; Kanti et al. 2004	Ethanol dehydration
		chitosan	Feng and Huang 1996; Goto et al. 1994	Ethanol, IPA, and ethylene glycol dewatering
	Inorganic	Microporous silica	Van Veen et al. 2001	Dewatering of IPA and 2-butanol
		Titania	Sekulic et al. 2002	Dehydration of IPA and 2-butanol
		Zirconia	Sekulic et al. 2002	Dehydration of IPA and 2-butanol
		ZSM-5	Bowen et al. 2004	Ethanol and IPA dehydration
		Mordenite	Bowen et al. 2004	Methanol, propanol, and IPA dehydration
		A-, X-, Y-, and T-type zeolite membranes	Bowen et al. 2004; Sommer and Melin 2005; Ying et al. 2004; Okamoto et al. 2001; Morigami et al. 2001	Ethanol dehydration
	Organic/inorganic	PDMS with zeolite filler	Vankelecom et al. 1995	Ethanol dehydration
		Chitosan-trimethoxysilane	Liu et al. 2005	Dehydration of IPA

Pervaporation Membrane, Table 2 Overview of membranes for hydrophobic pervaporation

Application	Membrane type	Membrane	References	Specific target
Removal of diluted organics	Polymeric	Poly(dimethyl siloxane) (PDMS)	Lipnizki et al. 1999; Mohammadi et al. 2005	Removal of chloroform, toluene, methylene chloride, trichloroethane, benzene, styrene, cyclohexane
		Polyurethane (PU)	Ji et al. 1994	Removal of toluene, trichloroethane
		Poly(ether-block-amide) (PEBA)	Djebar et al. 1998; Ji et al. 1994; and Peng et al. 2003	Removal of trichloroethane, methyl chloride
		Nitrile-butadiene rubber (NBR)	Brun et al. 1985	Removal of chloroform and toluene
		Styrene-butadiene rubber (SBR)	Brun et al. 1985	Removal of chloroform and toluene
		Supported ionic liquid membranes (SILMs)	Izák et al. 2003	Removal of toluene from toluene/alcohol mixtures
		poly [1-(trimethylsilyl)-1-propyne] (PTMSP)	Claes et al. 2011	Ethanol/water
	Inorganic	Silicalite membranes	Bowen et al. 2004	Ethanol removal from water

Pervaporation Membrane, Table 3 Overview of membranes for organophilic pervaporation

Organic-organic separations	Polymeric	Polyimide copolymer membranes	Ho et al. 1998	Separation of aromatic/saturated mixtures
		Polyetherimide segmented copolymer	Tanihara et al. 1994, 1995	Separation of benzene/cyclohexane, benzene/heptane, acetone/cyclohexane
		Polyimide-co-polyphenylenediamine	Tanihara et al. 1994, 1995	Separation of benzene/cyclohexane, benzene/heptane, acetone/cyclohexane
		Blended cellulose acetate and polyphosphonates	Cabasso 1983	Separation of benzene/cyclohexane
		Blended cellulose acetate and polybromophenylene oxide dimethylphosphonate ester	Acharya et al. 1988	Separation of benzene/cyclohexane
		Polypropylene PP	Villaluenga and Mohammadi 2000	Separation of benzene/cyclohexane
		Polyvinylidene fluoride (PVDF)	Villaluenga and Mohammadi 2000	Separation of benzene/cyclohexane
		Polymethyl methacrylate (PMMA)	Villaluenga and Mohammadi 2000	Separation of benzene/cyclohexane
	Organic/inorganic	Alumina supported PVA	Yoshida and Cohen 2003	Separation of methanol/MTBE

zeolite A is used as a molecular sieve for pervaporation. Because of the well-defined structure of the zeolites, very high separation factors can be obtained with zeolite membranes. The separation is then based on size effects rather than polarity effects.

Hydrophobic membranes are summarized in Table 2. They have a contact angle between 90° and 120°. The typical polymer for hydrophobic pervaporation membranes is polydimethylsiloxane (PDMS). A typical application of hydrophobic pervaporation is the recovery of ethanol from a fermentation broth. Given the low concentrations of ethanol usually encountered, this requires a multistep approach.

Organophilic pervaporation is in an earlier stage of development because the separation is more challenging, and membranes for specific solvent separations are still scarce. Nevertheless, this is a highly promising membrane type in view of many applications, ranging from solvent recycling to solvent exchange in e.g., pharmaceutical production (Table 3).

A general problem for the stability of a membrane in pervaporation is the effect of the vacuum applied at the permeate side. The vacuum is needed to obtain a sufficient difference in partial pressure. In such conditions, the membrane is not swollen. In contrast, the membrane is in contact with the liquid feed mixture at the feed side, which causes swelling by uptake of solvent. The more flexible the polymeric chains are (e.g., linear polymers), the more the membrane swells at the feed side. This causes an asymmetric structure (swollen/unswollen), which causes mechanical stress that might lead to cracking. Swelling can be avoided by crosslinking of the polymer, but a balance is needed because crosslinking usually has a negative impact on fluxes.

Cross-References

- Dense Membranes
- Macroporous, Mesoporous, and Microporous Membranes
- Pervaporation (PV)

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Pervaporation Membrane Reactor

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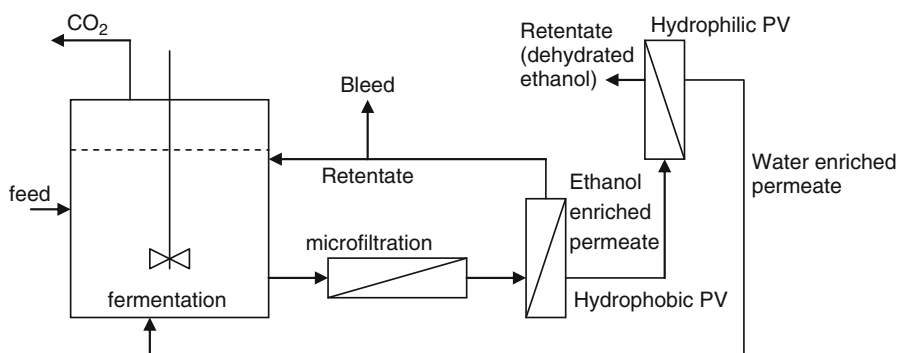
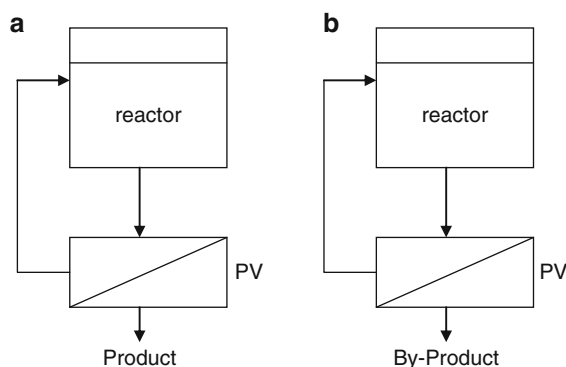
A pervaporation membrane reactor (PMR) is an integrated reaction-separation system, in which one or more components from a reaction medium is selectively removed in order to increase the yield of the reaction (Van der Bruggen 2010). The component removed by pervaporation can be the product (type 1 PMR) or a by-product (type 2 PMR). This is schematically shown in Fig. 1 (Lipnizki et al. 1999).

Pervaporation membrane reactors can be used for bioconversions (type 1 PMR), such as the production of bioethanol and bio-butanol, and for the extraction of aroma components from a fermentation broth. Vane (2005) describes a pervaporation-bioreactor hybrid process for ethanol fermentation and further ethanol purification by dehydration (Fig. 2). A hydrophobic membrane is needed for ethanol extraction (polydimethylsiloxane membranes are typical for this application), followed by a hydrophilic membrane for obtaining a sufficient ethanol purity.

Another type of applications is in conversion reactions limited by the chemical equilibrium. According to the principle of Le Châtelier-Braun, selective removal of a by-product in the

Pervaporation Membrane Reactor,

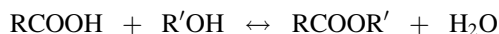
Fig. 1 (a) Type R1 PMR (removal of reactor product) and (b) type R2 PMR (removal of by-product) (Lipnizki et al. 1999)



Pervaporation Membrane Reactor,
Fig. 2 Fermentation reactor coupled to hydrophobic pervaporation for ethanol extraction, with microfiltration

pretreatment, and dehydration with hydrophilic pervaporation (Adapted with permission from Vane (2005))

reaction shifts the reaction equilibrium to a higher product yield (type 2 PMR). A typical class of reactions in which this is applied is esterification:



The most simple esterification reaction is the reaction of ethanol with acetic acid to yield ethyl acetate and water. To enhance the yield of RCOOR' (ethyl acetate in the example), H₂O can be removed by a hydrophilic pervaporation membrane (Datta and Tsai 1995; Waldburger and Widmer 1996). The membrane to be used should be hydrophilic, often based on polyvinyl alcohol (PVA). Other materials include polyvinylalcohol/polyacrylonitrile (PVA/PAN), polyetherimide (PEI), and 4,4'-oxydiphenylene pyromellitimide (POPMI) (Van der Bruggen 2010). Ceramic pervaporation membranes have specific advantages (more robust and higher fluxes, although

more expensive). For this application, a pervaporation membrane reactor is an alternative to the more conventional (and more energy-consuming) reactive distillation.

Pervaporation membrane reactors can be even more integrated by using a catalytically active inorganic pervaporation membrane, which acts both as catalyst and separator. An acid zeolite, H-ZSM-5, was used in what was called an "active zeolite membrane reactor (AZMR)." Gao et al. (1996) and Tanaka et al. (2001) studied the esterification of acetic acid and alcohol, catalyzed by an exchange resin, using a zeolite A-PVA composite membrane, and a zeolite T membrane, respectively.

In spite of many applications already studied, transesterification reactions have not yet been extensively considered. Many esters are made using transesterification, because the milder conditions prevailing permit the reaction of

components containing additional functional groups. In alcoholysis, a complex alcohol is reacted with a methyl ester, forming a complex ester and methanol. These reactions are all equilibrium limited and are therefore candidates for use in a pervaporation membrane reactor. However, pervaporation membranes needed for this type of PMR should be organophilic, which is more challenging than classical solvent-water separations. Nevertheless, membranes for specific conditions (in particular with methanol selectivity) have been reported and can be used (Bhat and Pangarkar 2000; Ray et al. 1999). The use of pervaporation membrane reactors for transesterifications in comparison with reactive distillation has also been described by Brinkmann et al. (2009).

Cross-References

- [Pervaporation \(PV\)](#)
- [Pervaporation Membrane](#)
- [Pervaporation-Assisted Reactor](#)

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Pervaporation Separation Factor

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The selectivity of a pervaporation membrane in a given separation is usually calculated by the dimensionless separation factor α . For a binary mixture consisting of components *A* and *B*, the separation factor α is given by the following equation, in which y_A and y_B are the permeate compositions and x_A and x_B are the feed or retentate compositions:

$$\alpha_{AB} = \frac{y_A/y_B}{x_A/x_B}$$

These compositions can be described by means of mole fractions, mass fractions, or volume fractions (Mulder 1996).

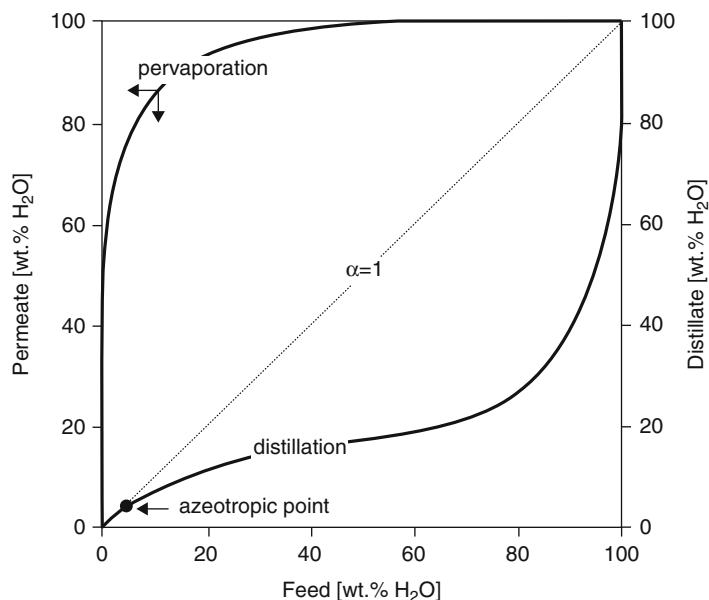
The separation factor is chosen in such a way that its value is greater than unity and so that component *A* permeates preferentially. If $\alpha = 1$, no separation can be achieved (composition of the feed is identical to the feed composition).

The separation factor in pervaporation is calculated in the same way as the relative volatility in distillation applications (vapor-liquid equilibrium). Because the separation in pervaporation is not obtained by effects of volatilization, however, the selectivity in pervaporation is very different than for distillation for the same binary system. In the figure below, the McCabe-Thiele diagram showing the vapor-liquid equilibrium and the

Pervaporation

Separation Factor,

Fig. 1 Comparison between selectivity in pervaporation (*upper curve*) and distillation (*lower curve*) (Kujawski 2000)



feed-permeate relation in pervaporation for the ethanol-water system is shown (Kujawski 2000). The composition of the feed mixture is shown on the x-axis; the y-axis gives the composition of the vapor in equilibrium with the respective liquid (for distillation) or the composition of the permeate (for pervaporation). The pervaporation membrane in the figure is a hydrophilic membrane through which water is passing preferentially (for any concentration of water) and is enriched in the permeate. The highest separation factor can be observed at low water content. Thus, pervaporation is ideal for removal of water from the feed mixture at low concentrations of water, in the case of water-ethanol mixtures. In distillation, on the other hand, the more volatile ethanol is enriched in the vapor phase at high water concentrations (below the azeotropic point). With decreasing water in the feed, the vapor-liquid equilibrium shows azeotropic behavior, which means that the composition of vapor and liquid are identical; (ordinary) distillation cannot be used to cross the azeotropic point (Fig. 1).

An alternative way to quantify selectivity is by the dimensionless enrichment factor β , which is defined as the ratio of the fraction (molar or mass) of component A in the permeate to the fraction of component A in the feed:

$$\beta_A = \frac{y_A}{x_A}$$

Usually, there is a trade-off between the permeation flux and selectivity; i.e., when one factor increases, the other decreases. As both of them are important numbers in the separation process, a pervaporation separation index (PSI) can be defined as a measure of the separation ability of a membrane (Sommer and Melin 2005):

$$\text{PSI} = J_{\text{tot}} \alpha_{AB}$$

in which α_{AB} is the separation factor as defined above, and J_{tot} is the total flux through the membrane.

Compared to other membrane processes, such as *ultrafiltration* and *reverse osmosis*, pervaporation generally has low fluxes ($<10 \text{ kg/m}^2\text{h}$). Nevertheless, its selectivity can be extremely high, with α often exceeding 1,000 for separation of components with a large difference in polarity. This is not the case for more difficult separations such as ethanol-water, for which separation factors are typically below ten; the highest reported separation factors for ethanol-water separation are in the order of magnitude of 20 (Claes et al. 2011).

Flux and selectivity are strongly influenced by the specific characteristics of the components in the feed, the membrane, and the process-operating parameters. These factors include permeate pressure, process temperature, feed composition and concentration, feed turbulence, membrane thickness, *concentration polarization*, *temperature polarization*, and the membrane material.

Cross-References

- [Temperature Polarization](#)
- [Ultrafiltration \(UF\)](#)

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Pervaporation Through Supported Liquid Membrane

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Supported liquid membrane pervaporation is a process for separating volatile organic compounds (VOCs) from their dilute aqueous solutions through a supported liquid membrane (Qin et al. 2002), often in a fermentation broth. It integrates simultaneous extraction of the VOCs from the aqueous solution with vacuum stripping of the

VOCs from the organic phase in one membrane module. The separation occurs by pervaporation, in which components selectively evaporate through a membrane. The membrane used in this case is a liquid membrane supported with a hydrophobic porous membrane (Matsumura and Kataoka 2004). The selectivity is thus determined by the choice of the liquid and its properties, and the selection of a proper liquid is a key factor for a successful separation. For example, oleyl alcohol was found to be the most suitable liquid for separating volatile products in ABE (acetone-butanol-ethanol) fermentation (Matsumura and Kataoka 2004). Oleyl alcohol is a preferred compound, since it is nontoxic to the microorganisms used in fermentation (Matsumura et al. 1992). The use of decanol (100 % pure) instead of oleyl alcohol (85 % pure) as the membrane solvent increased the flux and improved the stability without significant loss of performance up to about 70 h (Clement and Hossain 1997). Ionic liquids are a logical alternative in view of the stability of the membrane. Among the ionic liquids that have been considered are 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate and tetrapropyl-ammonium tetracyanoborate (Izak et al. 2009) and tetracyanoborate and tris(pentafluoroethyl)trifluorophosphate (Heitmann et al. 2012), but the range of ionic liquids that can be used for this purpose is very wide. For example, Matsumoto et al. (2011) studied pervaporation of 1-butanol and isopropyl alcohol (IPA) through a poly vinyl chloride membrane (PVC) as the active layer and a porous hydrophobic polyvinylidene fluoride membrane as the support layer for a series of ionic liquids, including Aliquat 336, Cyphos 101, 102, and 104. It has been shown that the sorption step mainly affected the separation factor depending on the hydrophilicity of the ionic liquid (Matsumoto et al. 2009).

Applications of pervaporation through supported liquid membranes are in the field of bioconversions. For example, an oleyl alcohol supported liquid membrane was successfully applied to diacetyl fermentation by immobilized lactic acid bacteria by Ishii et al. (1995). Diacetyl productivity was about 10 g per m³ and per h, while the productivity during batch fermentation

was about 6 g per m³ and per h. The diacetyl yield from consumed glucose was about four times as large as that of batch fermentation. No fouling effects were encountered by using the actual fermentation broth: the flux of the permeate and the diacetyl separation factor for the pervaporation were maintained at almost constant levels during fermentation. The diacetyl concentration in the permeate, which was about 2 kg/m³, was found sufficiently high for commercial use.

A closely related process is vapor permeation through supported liquid membranes, which is applied in, for example, the separation of benzene and cyclohexane (Matsumoto et al. 2009). The difference is in the feed solution, which is a liquid for pervaporation and a vapor for vapor permeation. The choice between both processes is not a fundamental difference but usually depends on the feed mixture to be separated.

A general challenge for supported liquid membranes is their stability during application. For aqueous applications, it was shown that the loss of the ionic liquid from the supporting membrane towards the contacting aqueous phases is not negligible (Fortunato et al. 2004). Matsumoto et al. (2009), however, obtained a steady flux and separation factor and suggest that the membrane was extremely stable in the application that was considered.

Cross-References

- [Pervaporation \(PV\)](#)
- [Supported Liquid Membrane](#)
- [Vapor Permeation](#)

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Pervaporation-Assisted Reactor

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Synonyms

[Pervaporation membrane reactor](#)

Reactors coupled with membrane separation, such as pervaporation, can help to enhance the conversion of reactants for thermodynamically or kinetically limited reactions via selective removal of one or more product species from the reaction mixture (Benedict et al. 2006). A pervaporation-assisted reactor is more frequently denoted as a pervaporation membrane reactor, and both terms are usually considered as synonyms. Pervaporation-assisted reactors are always described as chemical reactors, in which a side

product is removed to shift the reaction equilibrium, and more specifically in the context of esterification reactions. In these reactors, a hydrophilic pervaporation membrane is used to selectively remove water, which is a non-desired side product of any esterification reaction (Datta and Tsai 1995). For example, ethanol and acetic acid react to ethyl acetate, with water as the side product to be removed. Esterification of acetic acid is also studied with other alcohols, with much attention for the reaction with butanol (Bitterlich et al. 1991). Other esterifications that have been studied include the reaction of propanol with propionic acid, the reaction of oleic acid with ethanol, the reaction of tartaric acid with ethanol, and the reaction of erucic acid with cetyl alcohol, among many others (Van der Bruggen 2010).

One important feature to optimize the design of pervaporation-assisted reactors (pervaporation membrane reactors) is the integration of catalysts into the membrane structure. Catalytically active pervaporation membranes are also called “bifunctional” membranes, i.e., catalytic and separative. The fixation of the catalyst to a membrane was proposed by Shah and Ritchie (2005), but the membranes originally proposed were microfiltration membranes (Van der Bruggen 2010). The membrane is then used both as catalyst and as a separator. Bernal et al. (2002) used a catalytically active inorganic pervaporation membrane for the same purpose, instead of a microfiltration membrane. An acid zeolite, H-ZSM-5, was used as a catalyst for esterification reactions (ethanol and acetic acid to produce ethyl acetate) in what was called an “active zeolite membrane reactor (AZMR).” De la Iglesia et al. (2006) followed the same approach and synthesized two-layered mordenite-ZSM-5 membranes for the same esterification reaction. Using a two-layered membrane, the catalytic activity and the hydrophilicity necessary to obtain a high flux are combined in a single structure.

Going beyond the classical esterification reactor, a pervaporation-assisted reactor for transesterification is an interesting but challenging extension. In a transesterification reaction, the side product is not water, but methanol; this implies that methanol is to be separated from the

reaction mixture. This is a much more difficult separation to achieve with regular pervaporation membranes. A new generation of organophilic membranes is appearing, which is thought to stimulate a wider scope of applications of pervaporation-assisted reactors/pervaporation membrane reactors, also for non-hydrophilic pervaporation separations.

A possible application of non-esterification pervaporation membrane reactors is the dehydration reaction of butanediol to form tetrahydrofuran (THF), catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Liu and Li 2002). Numerous other reactions are of potential interest for enhancement in a pervaporation-assisted reactor. Several are described in the literature; for an overview, the reader is referred to Van der Bruggen (2010). The requirements are as follows: (a) it concerns an equilibrium reaction and (b) the by-product formed in the reaction can be selectively removed by a pervaporation membrane.

Cross-References

- [Pervaporation \(PV\)](#)
- [Pervaporation Membrane](#)
- [Pervaporation Membrane Reactor](#)

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Pervaporation-Based Hybrid System

► Pervaporation Hybrid System

Petrochemical Industry and Membrane Operations

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Petrochemical Industry includes different processes which, by means of chemical conversion and physical separations, produce a range of products, such as light olefins and aromatics, from the petroleum. Stringent environmental standards were important drivers for membrane implementation in the petrochemical/refinery processing, in a scenario of declining natural resources, for environmental and economic sustainability (Bernardo and Drioli 2010). Membrane systems can replace or can be integrated with conventional separation techniques (e.g., distillation, extraction, absorption, and adsorption), owing to modularity, low footprint, low energy intensity, no moving parts, and no need for solvents.

Polymeric membranes are available to recover valuable products like hydrogen and light hydrocarbons (ethylene, propylene and LPG) from refinery off-gas streams, or to produce nitrogen for inerting tanks. Hydrogen recovery from refinery tail gases had a rapid growth, owing to an

increased demand of hydrogen to desulfurize feedstocks and liquid heavy fractions. An increasing number of vapor/gas membrane systems are installed for gasoline vapor recovery at truck loading and retail gasoline stations or for the recovery of olefins and their recycle in the polyolefin production, thus reducing air pollution and achieving fuel savings (Baker et al. 1998). Plasticization-resistant perfluorinated membranes were specifically developed for these applications (Pinnau et al. 2002).

Organic solvent nanofiltration had the first large-scale application in solvent recovery from the dewaxing in lube oils processing, reducing the amount of crude oil required to produce a given volume of lube base stock and the loss of dewaxing solvents (Bernardo and Drioli 2010). It is also applied to remove tar components in FCC feed (Vandezande et al. 2008). Pervaporation allows to dehydrate solvents without the use of any third substance and to split azeotropes (Wynn 2001) and could effectively separate aromatic/nonaromatic hydrocarbon mixtures, as in the production of cyclohexane, to remove the unreacted benzene and to recover pure cyclohexane (Ye et al. 2008).

Wastewater treatment is one of the most important applications of membranes in the petrochemical field, meeting the increasing water quality standards prior to discharge, although these applications present challenging effluent streams. Stricter effluent regulations and increasing need for reuse/recycling of treated water were important drivers for implementing the membrane bioreactor (MBR) system in the petrochemical and refining industries with economic and environmental benefits. The MBR, combining the traditional biological degradation with a low-pressure membrane filtration, is an intensified process, with low space requirements and low visual impact, allowing to recycle water and reduce effluent discharge. In refineries, the highly treated wastewater can be reused in the crude processing, as cooling tower makeup, as boiler feedwater, or for other utility purposes. Recently, different refineries in Saudi Arabia and in the Middle East began to sell the treated water for irrigation (Bernardo and Drioli 2010).

The largest waste stream generated in oil and gas industries, referred to as produced water, is brought to the surface with oil (Ahmadun et al. 2009). The water stress in regions with freshwater scarcity is a strong driver to reclaim the produced water as potable and usable for agriculture irrigation, or alternatively in enhanced oil recovery. In this way, the petroleum industry could become a producer of freshwater. Produced water is typically saline; thus, it can be processed by a pretreatment followed by MBR treatment and reverse osmosis (Bernardo and Drioli 2010).

Integrated membrane systems offer the possibility of redesigning the energy-intensive refining/petrochemical industry, as proposed in an ethylene production cycle by steam cracking (Bernardo et al. 2004). The integration of different membrane systems (microfiltration, gas separation, membrane contactors) has shown the potential to reduce exergy with respect to conventional separation methods. This strategy would allow to develop new process concepts, improving the material utilization by a separation/recycle approach, reducing at the same time chemicals, energy/utility consumption, and waste stream production in refineries for clean fuel production and other important petrochemical productions.

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Phasing Methods in Crystal Structure Determination

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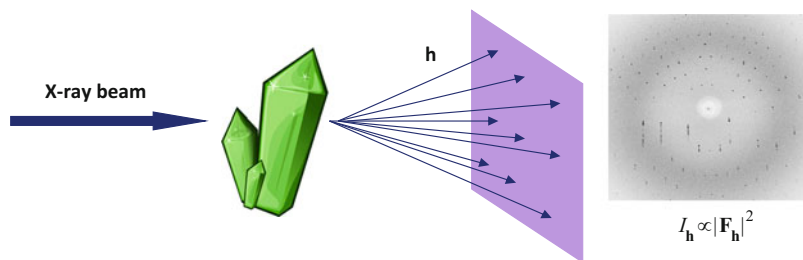
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Crystals obtained by membrane crystallization processes can be structurally investigated by means of Crystallography. The crystal structure can be determined by means of a diffraction experiment, which is outlined in Fig. 1. A crystal sample is irradiated by an intense X-ray beam, and the intensity of each reflection $\mathbf{h}$, representing a given direction of the scattered X-ray beam, is collected by an area detector. The intensity $I_{\mathbf{h}}$ is proportional to the modulus of the structure factor $F_{\mathbf{h}}$, which is a complex quantity, representing the response of the crystal system to the X-ray perturbation. However, to rebuild the image of the crystallized compound and then determine its structure, the phases $\varphi_{\mathbf{h}}$ of the structure factors are also necessary. In fact they depend on the positions of the atoms in the crystal cell. Thus, the phase problem consists in determining the phase of structure factors from their moduli. It can be solved by different computational methods, called “phasing methods”.

They can be classified as in Fig. 2. If measured intensities are the only information available, they are called *ab initio* methods; the most popular ones are direct or Patterson methods. The first works in the reciprocal space and makes use of

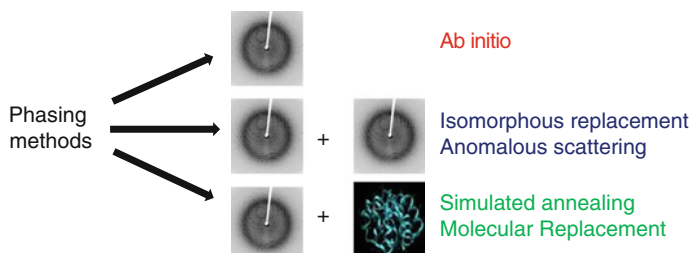
Phasing Methods in Crystal Structure Determination,

Fig. 1 Schematic view of a diffraction experiment



Phasing Methods in Crystal Structure Determination,

Fig. 2 Classification of existing phasing methods



the quantities $F_{\mathbf{h}}$ and $\varphi_{\mathbf{h}}$; the latter operates in the direct space and makes use of the electron density maps $\rho(\mathbf{r})$. Direct and reciprocal spaces are dual spaces, and their related quantities are connected by the relations:

$$F_{\mathbf{h}} = T[\rho(\mathbf{r})] \quad (1)$$

$$\rho(\mathbf{r}) = T^{-1}[\mathbf{F}_{\mathbf{h}}] \quad (2)$$

where T and T^{-1} denote the Fourier transform and anti-transform, respectively (Giacovazzo 1998). More recently, dual-space approaches have been developed, which work in both direct and reciprocal space.

Direct Methods

Direct methods allow extracting phase values directly from the observed structure factors moduli. They use a probabilistic approach (Hauptman 1975; Giacovazzo 1980) and are based on two general assumptions: the positivity of the electron density map and its atomicity, i.e., the fact that the electron density is not evenly distributed in the cell but is concentrated at the atomic positions.

Patterson Deconvolution Methods

The moduli of the structure factors contain information on the interatomic vectors of the crystal structure. This information can be made visible by calculating the Patterson map, through equation $P(\mathbf{u}) = T[F_{\mathbf{h}}^2]$. An ideal Patterson map can be interpreted as formed by the superposition of N images of a structure of N atoms, each shifted relative to the other by an interatomic vector (Buerger 1959). The recovery of a single image from the set of overlapping images can be accomplished by deconvolving the Patterson map, through vector superposition procedures (Caliandro et al. 2007).

Dual-Space Approaches

They are based on the assumption that a crystal structure is confined in a small region of the unit cell with high positive density; the rest of the map may be represented by large plateaus of negligible density. Constraints are imposed in each space: in direct space, specific modifications are applied to the electron density map, and in reciprocal space, calculated phase values are associated with

observed structure factor amplitudes to produce a new map. They are the charge flipping (Oszlányi and Sütö 2008) and *Vive La Différence* (Burla et al. 2010a, b) methods.

Non-Ab Initio Phasing

If instead additional information is available, the phasing methods are not ab initio. They are called isomorphous replacement when a derivative crystal containing heavy atoms is used or anomalous dispersion when the resonant scattering of some atoms of the structure is used (Giacovazzo 1998). If instead the approximate structural model is a priori known, the approach consists in searching for the best position and configuration of the structural model within the unit cell, driven by the agreement with experimental data. In case of small molecules, a global optimization search is used (Kirkpatrick 1984), and the uncertainty about the structural model is parameterized so that a flexible model is used within the search procedure (Favre-Nicolin and Černý 2002; Altomare et al. 2003). In case of macromolecules, the configuration of the structural model is not changed, and special vector search procedures, called molecular replacement, are used to place it in the unit cell (Rossman 1972).

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Phenol Degradation Using Membrane Reactor

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Phenol is one of major pollutants in industrial wastewater with high remediation priority. In the following a summary of some studies concerning phenol degradation in membrane reactors is reported.

Wastewater from coal gasification has poor biodegradability and high toxicity. A laboratory-scale anaerobic-anoxic-oxic membrane reactor (AAO-MBR) system was developed to investigate the treatment ability of coal gasification wastewater by Wang et al. (2012). The removal capacity of each pollutants used in this system was determined at different hydraulic residence times (HRT) and mixed liquor recycle ratios (R). The experimental results showed that this system could effectively deal with COD and phenol removal and remained in a stable level when the operational parameters were altered, while the nitrification was sensitive to operational conditions. The best performance was obtained at

HRT of 48 h and R of 3. The maximum removal efficiencies of COD, $\text{NH}_4^+\text{-N}$, and phenols were 97.4 %, 92.8 %, and 99.7 %, with final concentrations in the effluent of 71 mg/L, 9.6 mg/L, and 3 mg/L, respectively. Organic degradation and transformation were analyzed by GC/MS (gas chromatography/mass spectrometry), and it was found that anaerobic process played an important role in degradation of refractory compounds.

The effect of salt concentration on the performance of a membrane bioreactor (MBR) for treating an olefin plant wastewater was investigated by Sadeghi et al. (2012). For this purpose, a lab-scale submerged MBR with a flat-sheet ultrafiltration membrane was used for treatment of synthetic wastewater according to oxidation and neutralization unit of olefin plant. The synthetic wastewater was adjusted to have 500 mg/L chemical oxygen demand (COD). Trials on different concentrations of sodium sulfate (Na_2SO_4) (020–000 ppm) in the feed were carried out under aerobic conditions in the MBR. The results showed that increasing the salt concentrations causes an increase in the effluent COD, phenol, and oil concentrations. These results are due to reduction of the membrane filtration efficiency and also decline in the microbial activity. But in all the trials, the effluent COD and oil concentration were well within the local discharge limit of 100 and 10 mg/L, respectively. These results indicate that the MBR system is highly efficient for treating the olefin plant wastewater, and although high salt concentrations decreased organic contaminant removal rates in the MBR, the effluent still met the discharge limits for treating the olefin plant wastewater.

In municipal wastewater treatment plant (WWTP) effluents, the problem due to the presence of micropollutants in wastewater which may be able to disrupt the endocrine system of some organisms has been faced by Abargues et al. (2012). The fate of the alkylphenols (APs) (4-(tert-octyl) phenol, t-nonylphenol, and 4-p-nonylphenol) and the hormones (estrone, 17 beta-estradiol, and 17 alpha-ethinylestradiol) in a submerged anaerobic membrane bioreactor (SAMBR) pilot plant and in a conventional-activated sludge wastewater treatment plant

(CTP) has been compared. The obtained results were also compared with those obtained in a previous study carried out in an aerobic MBR pilot plant. The results showed that the AP soluble concentrations in the SAMBR effluent were always significantly higher than those in the CTP. Moreover, the analyses of the suspended fraction revealed that the AP concentrations in the SAMBR reactor were usually higher than in the CTP reactor, indicating that under anaerobic conditions, the APs were accumulated in the digested sludge. The aerobic conditions maintained both in the CTP system and in the aerobic MBR that favored the AP and hormone degradation and gave rise to lower concentrations in the effluent and in the reactor of these systems. Furthermore, the results also indicated that the degradation of APs under aerobic conditions was enhanced working at high solid retention time (SRT) and hydraulic retention time (HRT) values.

Direct coupling of separation and photocatalytic degradation by using photocatalytic membrane is an attractive way to solve problems like membrane fouling by adsorbed organic macromolecules or elimination of small organic molecules which cannot be efficiently stopped by a membrane. A simple and robust synthesis route to a photocatalytically active titania membrane was developed from a commercial TiO_2 hydrosol and commercial alumina supports by Djafer et al. (2010). Reproducible defect-free layers with a thickness of about 3 μm were prepared. The membrane performance in term of separation and photocatalytic activity was investigated. The pure water permeance was $150 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$ and the measured molecular weight cut-off was around 50 kDa corresponding to an ultrafiltration membrane. The photocatalytic efficiency was tested by photooxidation under UV irradiation of a reference organic dye (methylene blue) for comparison with reference TiO_2 photocatalysts and also with phenol as typical organic pollutant in water. The measured values of quantity of destroyed organic molecules per units of time and of membrane surface area are in the range $0.8\text{--}3.8 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$.

Phenol decomposition was carried out under UV irradiation in a recycle batch photocatalytic membrane reactor (PMR) by Yang et al. (2011).

To overcome the problem of post-recovery of the catalyst particles after water treatment, surface modification of polypropylene macroporous membrane was performed with the technique of photoinduced reversible addition-fragmentation chain transfer grafting polymerization of acrylic acid. TiO_2 photocatalysts were introduced into the acrylic acid-grafted membrane surface. In the tests on the PMR, the normalized membrane flux reached 1.7 times that of the unmodified membrane for the poly(acrylic acid) (PAAc)-modified membrane. Introducing TiO_2 photocatalysts into the membrane surface reduced slightly the normalized membrane flux. For the PMR with a grafting degree of 12.9 % (wt) of PAAc on the membrane surface, the corresponding decomposition percentage was 32.5 % after 6 h UV light irradiation.

The role of membrane in phenol degradation in high-phenol-fed MBR (membrane bioreactor) was explored by Ahn et al. (2011). Phenol elimination in high-phenol-fed MBRs resulted in complete mineralization, and the high-phenol-fed MBR exhibited greater biomass-specific phenol removal rates (0.4–1.5 mg phenol/(mg VSS.d)) than the low-phenol-fed MBR. In the high-phenol-fed MBR, filamentous non-settling microbes were more abundant than in the low-phenol-fed MBR. Batch experiment, high-acclimated, and non-settling microbes were separately collected from the high-phenol-acclimated bioreactor, and their specific phenol degradation was determined at 5.1 mg phenol/(mg VSS.d). The greater specific phenol degradation rate of the non-settling microbes than the observed phenol elimination rate in the high-phenol-fed MBR indicated that the high-phenol-acclimated and non-settling microbes had greater degradation activity than the rest of sludge microbes in the bioreactor. According to these findings, the role of membrane in the high-phenol-fed MBR was identified as the containment of non-settling and biodegradative microbes in bioreactor, and in turn, the membrane-driven increase of non-settling phenol degrading microbes enhanced phenol elimination in the high-phenol-fed MBR.

A novel process to biodegrade phenol present in an acidic (1 M HCl) and salty (5 % w/w NaCl)

synthetically concocted wastewater was studied by Livingston (1993). The process utilized a membrane bioreactor, in which the phenol present in the wastewater was separated from the inorganic components by means of a silicone rubber membrane. Transfer of the phenol from the wastewater into a biological growth medium allowed biodegradation to proceed under controlled conditions which were unaffected by the presence of inorganic species in the synthetic wastewater. At a wastewater flow rate of 18 mL h^{-1} (contact time 6 h), 98.5 % of phenol present in the wastewater at an inlet concentration of $1,000 \text{ mg L}^{-1}$ was degraded; at a contact time of 1.9 h, 65 % of the phenol was degraded. Phenol degradation was accompanied by growth of a biofilm on the membrane tubes and by conversion of approximately 80 % of the carbon entering the system to CO_2 carbon. Analysis of the transport of phenol across the membrane revealed that the major resistance to mass transfer derived from the diffusion of phenol across the silicone rubber membrane. A mathematical model was used to describe the transfer of phenol across the membrane and the subsequent diffusion and reaction of phenol in the biofilm attached to the membrane tube. This analysis showed that (a) the attached biofilm significantly lowers the mass transfer driving force for phenol across the membrane, and (b) oxygen concentration limits the phenol degradation rate in the biofilm. These conclusions from the model are consistent with the experimental results.

The effect of adaptation of mixed culture in the phenol biodegradation was studied by Marrot et al. (2006). The degradation experiments were carried out at different phenol concentrations from 0.5 to 3 g L^{-1} . Biological treatment showed to be economical and practical leading to a complete removal of phenol. High concentrations of phenol were inhibitory for growth, so it was for the rates of substrate utilization that were greater at low initial concentrations. Haldane kinetics model for single substrate was used to obtain maximum specific growth rates ($\mu_m = 0.438 \text{ h}^{-1}$), half saturation ($K = 29.54 \text{ mg L}^{-1}$), and substrate inhibition constant ($K_{-i} = 72.45 \text{ mg L}^{-1}$). These results were in agreement with those reported in the literature for phenol removal abilities in different systems,

although the concentration in phenol was significant, and the Haldane model was acceptable.

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Phenol Production by Membrane Reactor

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The great interest in the oxidation reaction of benzene to phenol is linked to some disadvantages of the cumene process, such as environmental impact,

production of an explosive intermediate and the fact that this is a multistep process that involves a low yield of phenol and a high capital investment. Moreover, the high acetone production as a coproduct, which results in an oversupply in the market, is another drawback. Various studies concerning a new approach based on a one-step and acetone-free method for phenol production have been reviewed by Molinari and Poerio (2010). Particular attention was devoted to phenol production processes using various configurations of membrane reactors (MRs) and a photocatalytic membrane reactor (PMR). In particular, the biphasic MR allowed to achieving high selectivity values (97–98 %). The various methods have been classified according to oxidant type such as N_2O , O_2 , and H_2O_2 . All of them indicated that direct oxidation of benzene to phenol is a difficult task and further efforts are needed to search and to replace the three-step traditional process with a process of direct oxidation to convert benzene in phenol.

Phenol production through the direct hydroxylation of benzene with hydrogen peroxide using a catalytic membrane reactor was studied by Molinari et al. (2006). The reaction was carried out in a biphasic system separated by a membrane. This new system showed a high selectivity to phenol, minimizing its overoxidation in overoxygenated by-products. The effect of various reaction parameters such as the addition of hydrogen peroxide mode, amount of hydrogen peroxide, type of membrane, type of catalyst, and organic acid was investigated. The results showed that iron(II) sulfate as the catalyst, 18 mmol of hydrogen peroxide pumped for 4 h in the aqueous phase as oxidant feeding, acetic acid and polypropylene hydrophobic porous support gave the best system performance in terms of produced phenol (17.42 mmol), selectivity to phenol (99.94 %), benzene conversion to phenol (1.20 %), and conversion of hydrogen peroxide to phenol (96.78 %).

Use of vanadium based catalysts and product recovery in benzene hydroxylation to phenol was studied in a two-phase membrane reactor by Molinari et al. (2012). Benzene permeates, through the hydrophobic polypropylene membrane, in the aqueous phase containing the

catalyst while phenol permeates back accumulating in the organic phase. The following fundamental aspects have been studied: dose of hydrogen peroxide, initial oxidation states of vanadium catalysts, duration of catalytic tests, and lifetime of the membrane in terms of physical and chemical resistance. It was observed that by feeding the oxidant by a micro pump, working in the “bulk tube” mode, phenol yield, final phenol concentration in the organic phase, phenol turnover number, and system productivity increased, and no tar was formed. Initial oxidation state of vanadium catalysts influenced system performance: indeed improved results in terms of yield (35.2 % vs. 25.1 %), conversion of hydrogen peroxide to phenol (36.6 % vs. 25.9 %), and productivity ($0.97 \text{ g g(cat)}^{-1} \text{ h}^{-1}$ vs. $0.78 \text{ g g(cat)}^{-1} \text{ h}^{-1}$) were obtained by using vanadium(III) chloride compared to vanadium(IV) acetyl acetonate. Higher phenol extraction/recovery in the organic phase (61.1 % vs. 46.3 %) and then higher selectivity (97.5 % vs. 92.8 %) were obtained by increasing test duration from 270 to 510 min. A weak membrane resistance was observed after 246 h of consecutive catalytic runs on the same membrane piece, showing degradation of the membrane material (polypropylene) caused by the OH radical generated in the reacting mixture.

The one-step hydroxylation of benzene to phenol with oxygen and hydrogen was studied by Shu et al. (2009). It is a promising process, but there are severe challenges associated with the low phenol production. It was shown that the reaction can be greatly promoted by the simultaneous use of a dense palladium membrane as a catalyst and as a hydrogen distributor. This reaction concept with palladium membranes was tested under different reaction conditions, but it was found that the palladium membranes were almost inert for both the target reaction and the benzene combustion. The authors summarized and compared their results with those reported in the literature investigating the effects of the membrane preparation method and the combustion of hydrogen and benzene. The hypotheses on the mechanism and feasibility of the membrane concept are also given.

A simple, low-cost design of glass capillary microreactor for the catalytic oxidation of benzene to phenol at ambient conditions was studied

by Basheer (2013). Polyvinylchloride-nanofiber-membrane-supported titania nanoparticles (TiO_2 -PVC) as catalyst was used by producing in situ hydroxyl radicals as oxidant. The reaction was monitored by gas chromatography–mass spectrometry (GC-MS). The reaction conditions were optimized and the performance of the microreactor was then compared with the conventional laboratory scale reaction which used hydrogen peroxide as oxidant. The microreactor gave a better yield of 14 % for phenol compared to 0.14 % in the conventional laboratory scale reaction. Reaction conditions such as reaction time, reaction pH, and applied potential were optimized. With optimized reaction conditions selectivity higher than 37 % and conversion of benzene higher than 88 % were obtained.

The study of a new reactor design with separate membranes for distributed dosage of hydrogen and oxygen, respectively, into microstructured reaction channels for the direct conversion of benzene to phenol in the gas phase in a palladium membrane reactor has been investigated by Bortolotto and Dittmeyer (2010). The highest phenol selectivity so far obtained on a palladium-coated PdCu foil at 423 K was 9.6 % with carbon dioxide being the dominant product.

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Phenol Recovery Using Membrane Contactor

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Phenol recovery from different aqueous solutions (industrial wastewater and process water) is of wide interest from environmental and industrial point of view. Among the various recovery processes, some of the involving membranes are described in the following.

The recovery of phenol from aqueous solutions with CYANEX (R) 923 was studied by Cichy et al. (2001). Classical dispersive extraction and three membrane extraction-stripping systems (bulk liquid membranes, three-phase hollow-fiber contactor, and two hollow-fiber module setup) were used. It was found that CYANEX (R) 923 was a convenient carrier for recovery of phenol from aqueous streams in extraction-stripping membrane processes. The problem of emulsion formation, so important in dispersive extraction, was avoided. Both mass-transfer experiments in different membrane systems and measurement of the dynamic interfacial tension demonstrated the importance of the interfacial phenomena occurring in the stripping stage. A blocking of this interface was observed that resulted in a decrease of phenol mass transfer.

Pertraction of dimethylcyclopropanecarboxylic acid (DMCCA) and phenol in a new hollow-fiber (HF) contactor of three liquid phases with distributed U-shaped bundles of microporous HF was studied by Schlosser et al. (2002). Trioctylamine (TOA), Hostarex A327, and Cyanex 47 1 X have been used as carriers. The performance of this contactor is similar to other HF contactors. Its advantage is that both bundles of fibers can elongate without deformation of fibers and maldistribution of fibers in the bundles. Pulsation of the membrane phase increases the transport rate by 35–61 %, and it reaches a plateau value at the pulsation velocity of about $1.1 \text{ mm} \cdot \text{s}^{-1}$.

With increasing velocity of the feed in the fiber lumen, the value of the overall mass-transfer coefficient increases, but soon a steady value is approached at the velocity of about $5.5 \text{ cm} \cdot \text{s}^{-1}$. The diffusion resistances in a series model do not describe the pertraction of DMCCA well. The suggested new diffusion-reaction model, considering the resistance based on the kinetics of the stripping reaction, fits experimental data well. Not only the rate of the acid-carrier complex decomposition but also that of the DMCCA dimer decomposition has to be considered. The estimated values of the apparent reaction rate constant were for the membrane with TOA $1.91 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1}$ and for pure *n*-alkanes $5.78 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1}$. The kinetic resistance on the stripping interface represents 20–60 % of the overall mass-transfer resistance, and its value is comparable to the diffusion resistance of both walls.

Application of membrane techniques (pervaporation and membrane-based solvent extraction) and adsorption to the removal of phenol from solutions modeling wastewater from phenol production by cumene oxidation process was investigated by Kujawski et al. (2004). The transport and separation properties of composite membranes PEBA, PERVAP 1060, and PERVAP 1070 in pervaporation of water-phenol mixtures were determined. It was found that the best removal efficiency of phenol was obtained using the PEBA membrane. MTBE, cumene, and the mixture of hydrocarbons were applied in the membrane-based phenol extraction. Extra-flow contactor with Celgard X-30 polypropylene hollow-fiber porous membranes was used in the experiments. MTBE was found the most efficient extractant. Adsorption of phenol on the different Amberlite resins was also investigated. Among the Amberlite resins of various grades used, the Amberlite XAD-4 had the best properties in the phenol removal from the aqueous solutions. It was shown that regeneration of the adsorbent bed could be effectively performed with sodium hydroxide solution.

The extraction and stripping of phenol using a solution of tributyl phosphate in kerosene in a hydrophobic polypropylene hollow-fiber membrane contactor was studied by Shen

et al. (2009). The effect of the aqueous and the organic phase flow rates on the overall mass-transfer coefficient for both extraction and stripping steps was investigated. Experimental values of the overall mass-transfer coefficient were determined and compared with predicted values from the resistance in series model. Results showed that the overall mass-transfer coefficients for extraction were about one order of magnitude greater than those measured during the stripping process. The experimental values were in good agreement with the predicted values for the extraction module. However, the predicted values were slightly overestimated for the stripping module. The individual mass-transfer resistances were analyzed, and the rate-controlling steps of mass transfer were also identified in both extraction and stripping modules. The major resistance in extraction and stripping was in the aqueous phase and in the membrane phase, respectively.

The removal of phenols from wastewater has been investigated under various operational conditions using hydrophobic hollow-fiber membrane contactors (Shen et al. 2012). Experimental overall mass-transfer coefficients were obtained in both handmade and Liqui-Cel™ modules. Model predictions based on a resistance in series model with solvent-filled membrane pores matched well with experimental values for tributyl phosphate/Shellsol extraction systems. However, the predictions were in poor agreement with experimental data obtained when 50 % pentanol/xylene was used to treat industrial wastewater in the handmade module. Further analysis showed that the operational pressure on the aqueous side and the breakthrough pressure for the two solvents probably influenced the position of the interface within the membrane pores. This change in wetting patterns resulted in significant differences in mass transfer and solute recovery which can be accounted for by adjusting the position of the interface within the membrane fiber.

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Phenol Separation on PV Membrane Reactor

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Phenol separation from different aqueous and nonaqueous solutions (industrial wastewater and process water) using pervaporation (PV) membranes is of wide interest from environmental and industrial point of view. In the following, applications of these membranes are described.

A general review on different membrane processes and membrane reactors in petrochemical industry, such as olefin/paraffin separation processes, light solvent separation, solvent dewaxing, phenol and aromatic recovery, dehydrogenation, oxidative coupling of methane, and steam reforming of methane were discussed in detail by Ravanchi et al. (2009). Besides, separation using polymer-inorganic nanocomposite membranes and wastewater treatment using membrane bioreactors are reported. The available technologies for the abatement of phenol from water and gaseous streams were briefly reviewed, and the recent advancements summarized by Busca et al. (2008). In this work separation technologies, such as distillation, liquid-liquid extraction with

different solvents, adsorption over activated carbons and polymeric and inorganic adsorbents, membrane pervaporation, and membrane-solvent extraction, are discussed. Destruction technologies such as non-catalytic, supercritical, and catalytic wet air oxidation; ozonation; non-catalytic, catalytic, and enzymatic peroxide wet oxidation; electrochemical and photocatalytic oxidation; supercritical wet gasification; destruction with electron discharges; as well as biochemical treatments are also considered. In particular, for the abatement of phenol from gases, condensation, absorption in liquids, adsorption on solids, membrane separation, and thermal, catalytic, photocatalytic, and biological oxidation are also described and the experimental conditions and performances of the different techniques compared.

Application of membrane techniques (pervaporation and membrane-based solvent extraction) and adsorption to the removal of phenol from solutions modeling wastewater from phenol production by cumene oxidation process was investigated by Kujawski et al. (2004a). The transport and separation properties of composite membranes PEBA, PERVAP 1060, and PERVAP 1070 in pervaporation of water-phenol mixtures were determined. It was found that the best removal efficiency of phenol was obtained using the PEBA membrane. MTBE, cumene, and the mixture of hydrocarbons were applied in the membrane-based phenol extraction. Extra-Flow contactor with Celgard X-30 polypropylene hollow-fiber porous membranes was used in the experiments. MTBE was found the most efficient extractant. Adsorption of phenol on the different Amberlite resins was also investigated. Among the Amberlite resins of various grades used, the Amberlite XAD-4 had the best properties in the phenol removal from the aqueous solutions. It was shown that regeneration of the adsorbent bed could be effectively performed with sodium hydroxide solution.

Application of pervaporation and adsorption to the removal of phenol from solutions modeling wastewater from phenol production with cumene oxidation process was investigated by Kujawski et al. (2004b). The transport and separation

properties of composite membranes PEBA, PERVAP 1060, and PERVAP 1070 in pervaporation of water-acetone, water-phenol, and water-phenol-acetone mixtures were determined. It was found that all membranes were selective toward phenol. The PEBA membrane showed the best selectivity. However, this membrane is not actually available on the commercial scale. Thus, in the practical applications, PERVAP-1060 and PERVAP-1070 could be used. Adsorption of phenol on the different Amberlite resins was also investigated. Among the Amberlite resins of various grades used, the Amberlite XAD-4 had the best properties in decontamination of aqueous phenol solutions. It was shown that regeneration of the adsorbent bed could be effectively performed with sodium hydroxide solution.

The separation of a phenol-water mixture using a polyurethane membrane by a pervaporation method was investigated by Hoshi et al. (1997). Polyurethane was selected as a membrane material because its affinity for phenol was considered to be high and was prepared by the polyaddition of 1,6-diisocyanatohexane and polytetramethyleneglycol. The polyurethane layer was sandwiched with a porous polypropylene membrane (Celgard[®] 2500). Pervaporation measurements were carried out under vacuum on the permeate side, and the permeate vapor was collected with a liquid nitrogen trap. The phenol concentration in the permeate solution increased from 0 to 65 wt.% with increasing feed concentration of phenol from 0 to 7 wt.%. The total flux also increased up to $930 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ with increasing phenol partial flux. In the sorption measurement at 60 °C, the concentration of phenol in the membrane was 68 wt.%, which was higher than that of the permeate solution.

The effect of the methylene group length in poly(alkylene glycols) on permselectivity and solubility of phenol was studied by Hoshi et al. (2000) in dilute aqueous solution through polyurethane membranes by pervaporation. The poly(alkylene glycols) were obtained by polycondensation of 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol with a sulfuric acid catalyst. Polyethyleneglycol and polytetramethyleneglycol were commercially available. Progress of the polymerization in the poly(alkylene glycols) was

confirmed by FTIR, ^1H -NMR analysis, and size-exclusion chromatography (SEC) measurements. The polyurethanes were obtained by polyaddition reaction of 1,6-hexamethylenediisocyanate and the poly(alkylene glycol) and were confirmed by FTIR analysis and SEC measurements. The phenol concentration in a permeate liquid increased from 25.1 to 36.2 wt.%, and the phenol partial flux also increased from 49.3 to 68.9 $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ with increasing the methylene group length in the poly(alkylene glycols), whereas the water partial flux slightly decreased. As a result of sorption measurements, the change in the degree of swelling was small, and the phenol concentration in the membrane increased from 42.1 to 70.8 wt.%. The increase in the methylene group length of the poly(alkylene glycols) should contribute to an increase in the hydrophobicity of the polyurethane so that the solubility of phenol to the membrane should increase. The phenol concentration in the permeate liquid and the phenol partial flux increased with an increase in the methylene group length of the poly(alkylene glycols) due to the increase in the phenol solubility for the polyurethane membranes.

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Phenolic Compound

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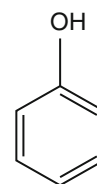
Phenolic compounds are a chemical class consisting by at least one aromatic ring (C6) bearing one or more hydroxyl groups. The hydrogen of the phenolic hydroxyl groups is labile thanks to the aromatic ring, which is responsible for the weak acid characteristic of phenols (Wermerris and Nicholson 2007). They are found in the natural world, being one of the most important groups occurring in the plant kingdom where they are the most abundant secondary metabolites in plants – usually found as esters or glycosides and not as free compounds. They are responsible for several functional activities in plant's life cycle including defense, attractants for pollinators, and protection against ultraviolet light (Jaganath and Crozier 2010). These characteristics explain their wide use commercially as flavoring agents, natural drugs, antioxidants, etc., acting as natural additives.

Phenol ($\text{C}_6\text{H}_5\text{OH}$) is the simplest compound of the class (also called carboic acid), and its structure is represented in Fig. 1. Polyphenols are compounds that have more than one hydroxyl group attached to one or more benzene rings.

It is possible to divide the phenols in several different groups according to the number of carbons in conjunction with the structure of the basic phenolic skeleton – simple phenols, phenolic acids, coumarins, phenylpropanoids, flavonoids, antocyanins, catechins, terpenoids, to highly polymerized compounds, such as condensed tannins. Their molecular weight is in the range of

Phenolic Compound,

Fig. 1 Basic structure of a phenol



90–350 g/mol. Flavonoids constitute the most important polyphenolic class, with more than 500 compounds already described.

These compounds are reported to exhibit anticarcinogenic, antiinflammatory, antioxidant, and antimicrobial activities, among others. Several studies were carried out in order to correlate the consumption of foods with high concentrations of polyphenols and the reduced risk of degenerative diseases, mostly with very positive results. For example, they can prevent neurodegeneration by trapping radicals, working as a preventive action. So, phenolic compounds presented a potential protective role through ingestion of fruits and vegetables, working against oxidative damage diseases (coronary heart disease, stroke, and cancers) (Jaganath and Crozier 2010).

Their antioxidant activities and the possibility of use in processed foods as a natural antioxidant are the explanation for the increased interest in phenolic acids. Their antioxidant properties come from their redox potential, which can act as free radical scavengers, hydrogen donors, metal chelators, and singlet oxygen quenchers. The effectiveness in food depends on not only the number and location of hydroxyl groups but also on factors such as physical location, interaction with other food components, environmental conditions (e.g., pH), and the degree of glycosylation – aglycons of quercetin and myricetin are more active than their glycosides (Marchand 2002). The most well-known physiological phenolic antioxidant is vitamin E.

Antimicrobial activity of phenolic compounds is related to the principle of inactivation of cell enzymes, what explains the different activities between Gram-negative and Gram-positive species once they have variations in their cell structures. The antimicrobial effect related with phenolic compounds contents in several natural products, as olive (Pereira et al. 2007), wine (Cueva et al. 2012), mushroom (Barros et al. 2007), propolis extracts (Hendi et al. 2011), and green tea (Kristanti and Punbusayakul 2009).

As every natural product, phenolic compounds have a great utilization potential in several processes in order to aggregate their main properties. It is important to know their action mechanisms

and utilization forms to produce better products with functional properties.

The use of membrane operations to separate, purify, and produce phenolic compounds from natural sources is very attractive due to the clean, safe, and low energy input of the technology

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Phosphate Removal from Water and Wastewater by Membrane Operations

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Phosphate (also referred as phosphorus in some literatures which in fact is one of its constituting

elements) is a vital constituent for plants, animals, and human. Under natural circumstances, the presence of phosphorus is rare in water. Human activities have, however, changed the natural picture. Phosphorus enters into freshwater through several sources originating from domestic, industrial, and agricultural wastes. Phosphorus is commonly present into aqueous solutions in forms of orthophosphate, polyphosphate, and organic phosphorus compounds. The type of phosphorus associated with each source is generally different. Leaching from naturally occurring mineral resources, food processing effluents, and lands enriched with fertilizers play a significant role in contaminating the water with phosphorus that gives rise to eutrophication defined as the excess of nutrients into a stream that deteriorates the quality of water by stimulating the excessive growth of plants. Eutrophication causes excessive growth of blue-green algae causing pollution problems. The situation becomes further complex when bacteria ingest dead algae leading to the elimination/deficiency of dissolved oxygen into the water and rise in concentration of nutrients and related organic compounds. The depletion of dissolved oxygen can affect the marine life destructively. On the other hand, toxic nature of the compounds produced by blue-green algae has been reported in some studies. The algal bloom has been indicated a big problem for portable water treatment plants. On the other hand, the primary source of phosphate is apatite, and its extraction process is highly energy intensive and causes environmental problems. Therefore, the development of a closed loop cycle for phosphorus by its removal and recycling has gained significant attention recently.

It is worth to note that only orthophosphate can be precipitated and separated from aqueous solution. Both biological and chemical treatments have been applied to lower down the phosphorus concentration into the effluent to its desired level. In chemical treatment, coagulant comprising of multivalent metal ions is mixed with the wastewater containing phosphate, and precipitates of inorganic phosphate are separated from the solution. Biological treatment comprises of anaerobic tanks placed upstream of an aeration tank. The

main objective is the selective enrichment of polyphosphate-accumulating organisms in the sludge. These bacteria possess the capability to accumulate a huge quantity of polyphosphate. The biomass can be separated from treated water at the end of the process. The conventional biological processes generally do not meet the required criteria. On the other hand, chemical treatment suffers the drawbacks of high chemical cost and large volume of sludge produced. Therefore, a combination of biological and chemical treatment is also applied to achieve desired level of 1–2 ppm established by most of the countries. Several new technologies to remove phosphate from wastewater have emerged. The main examples include calcium-sequestered phosphate removal, magnetic separation, and adsorption.

Recently, some attentiveness has been observed in application of membrane operations to treat wastewater containing phosphate, mainly due to their capability to achieve an effluent of very high quality (as low as 0.008 ppm of phosphorus). Both suspended and dissolved forms can be removed by using membrane techniques. Reverse osmosis and nanofiltration have been applied to treat the effluents containing phosphorus. Thanks to the capability of the processes to remove multivalent and monovalent ions, very high phosphorus removal efficiency can be achieved (Lee et al. 2014). On the other hand, the retentate contains phosphorus in much concentrated form causing the disposal issues. The biological and chemical treatments traditionally apply gravity clarifiers and filtration separation which are insufficient to separate all chemical and biological entities present and cannot capture all the phosphate. Traditional operations have been integrated with membrane-based separation to achieve small footprint and decoupling of hydraulic retention time from solid retention time and to improve the effluent quality. Membrane bioreactors, tertiary membrane operations, and RO have been applied in large-scale installations, and attractive results have been achieved. Innovative membrane operations including forward osmosis, membrane distillation, and electrodialysis are being investigated for phosphorus removal from various waste streams. Some

studies also report a high process cost related with membrane operations (Jiang et al. 2004). The interest in membrane-based operations lies not only in purifying the water but also in recovering the phosphorus and reintroducing it into the cycle.

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Photocatalysis with Membrane Distillation

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Photocatalysis by polycrystalline semiconductor oxides is being successfully applied to the abatement of organic and inorganic pollutants both in gas and in liquid phases. In order to increase the efficiency of this method, the coupling of this technology with the membrane separation process has been the object of investigation. In this combination, the membrane may act in different ways: to confine the photocatalytic powder in the reacting suspension, to selectively separate the photoreaction products, or to be the support of photocatalyst. Recent studies in which different types of membranes (such as distillation, dialysis, nanofiltration, pervaporation, and osmosis membranes) were used in hybrid systems have been reviewed by Loddo et al. (2009) describing perspectives and future possible application of the synergy between membranes and photocatalytic reactors. An additional advantage of coupling is

that the photocatalyst prevents the microbial fouling offering a strong potential for the use of new types of thin-film-composite membrane.

In the following, some studies concerning in details the application of photocatalysis and membrane distillation are reported.

To solve problems concerning separation of photocatalyst as well as products and byproducts of photodecomposition from the reaction mixture, the application of photocatalytic membrane reactors (PMRs) is a promising method. The PMRs described in literature combine photocatalysis with pressure-driven membrane techniques, such as nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). A serious problem with application of these membrane techniques can be membrane fouling, which is especially observable with MF and UF. The results of the investigation on the possibility of coupling photocatalysis and membrane distillation (MD) for degradation of organic pollutants in aqueous solution were described by Mozia et al. (2005). Acid Red 18 was applied as model dye and titanium dioxide Aeroxide (R) P25 (Degussa, Germany) was used as photocatalyst. In the first step of the research, the effect of the presence of TiO_2 in a feed on the permeate flux was investigated. It was found that the addition of TiO_2 P25 did not affect the distillate flux, regardless of the catalyst concentration applied. In order to select the best process conditions in terms of photocatalyst concentration and temperature of feed solution batch tests were performed. On the basis of these experiments, TiO_2 concentration and feed temperature in the reactor were set at 0.3 g/dm^3 and 333 K, respectively. The hybrid process photocatalysis -MD was conducted in a simultaneous mode. After 5 L of permeate the model dye was removed completely, whereas total organic carbon (TOC) concentration was lowered down to 20 % of the initial value.

Mozia et al. (2007) investigated on the possibility of coupling photocatalysis and direct contact membrane distillation (DCMD, MD) for degradation of azo dyes (Acid Red 18, Acid Yellow 36, and Direct Green 99) in aqueous solution. TiO_2 Aeroxide (R) P25 (Degussa, Germany) was used as the photocatalyst. It was found that the

addition of TiO₂ P25 to the feed did not affect the distillate flux, regardless of the catalyst concentration applied. The MD process was very effective in separation of photocatalyst particles. After 5 h of the experiment, the turbidity of distillate was similar to that measured for ultrapure water, regardless of the TiO₂ loading used. The highest effectiveness of photodecomposition was obtained in case of Acid Red 18, whereas Acid Yellow 36, which has the lowest molecular weight among the dyes used, was degraded with high difficulty. The composition of the feed solution slightly influenced the quality of distillate. Among the volatile compounds that passed through the membrane, some organic compounds were present as indicated by the measurements of TOC concentration.

An anatase-phase TiO₂ was applied for degradation of Acid Yellow 36 (AY36) in the PMR coupling photocatalysis and direct contact membrane distillation (DCMD) by Mozia et al. (2009). The effect of different process parameters such as dye concentration, reaction temperature, and photocatalyst loading on the effectiveness of degradation of AY36 was investigated. Moreover, in order to compare the effectiveness of AY36 photodegradation during photocatalysis alone and the hybrid process, additional experiments without application of the membrane distillation (MD) were conducted. The addition of TiO₂ to a feed did not affect the permeate flux, regardless of the process conditions applied. The latter remained constant during about 400 h of experiments. The highest decolorization of AY36 solution during hybrid process was observed at the highest photocatalyst loading applied (0.5 g TiO₂/dm³). The increase of the reaction temperature from 313 to 333 K resulted in an increase of the photodegradation rate of AY36. After 5 h of the hybrid process, the effectiveness of dye degradation calculated on a basis of AY36 mass in a feed solution amounted to 31 %, 36 %, and 42 % at reaction temperatures 313–333 K. Similar results were obtained when photocatalysis was conducted in the MD installation but with the MD module disconnected. An improvement of AY36 photodegradation was achieved by decreasing the initial dye

concentration. The best configuration seemed to be the PMR one by taking into account the rate of azo dye degradation and the quality of the product.

The investigations on the photodegradation of a nonsteroidal anti-inflammatory drug ibuprofen sodium salt (IBU) in a photocatalytic membrane reactor (PMR) coupling photocatalysis using suspended TiO₂ and direct contact membrane distillation was also described by Mozia et al. (2012). The influence of solution composition in terms of (i) pH (pH 3, pH 6.5, and pH 10), (ii) presence of inorganic salts (NaCl, Na₂SO₄, NaHCO₃, NaNO₃, and Na₃PO₄), and (iii) turbidity (bentonite, 13.5–103 NTU) on the effectiveness of IBU removal was especially investigated. The highest effectiveness of IBU photodegradation was obtained at pH 6.5. No influence of the presence of NaCl, NaNO₃, and Na₂SO₄ on the effectiveness of degradation and mineralization of IBU was found. NaHCO₃ and Na₃PO₄ did not affect the effectiveness of degradation of IBU; however, the efficiency of mineralization decreased significantly. The increased turbidity of feed solution did not affect IBU removal in the PMR.

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Photocatalyst

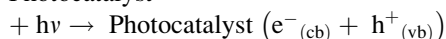
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Photocatalyst can be defined as a substance that is able to produce, by absorption of ultraviolet, infrared, or visible light, chemical transformations of reaction partners, repeatedly coming with them into various chemical interactions without the occurrence of a permanent modification of its chemical composition. After each cycle of interaction between the reagent(s) and the photocatalyst, the chemical composition of the last is regenerated. The presence of a photocatalyst gives rise to an enhancement of the rate of a chemical reaction or its initiation under ultraviolet, infrared, or visible light illumination, and the role of light is to photo-excite the solid that works as the photocatalyst (Braslavsky et al. 2011). Notably, in some cases, light can be absorbed by the adsorbed reacting species that can be transformed and the solid photocatalyst works only as an adsorbent.

The materials that are generally used as photocatalysts are semiconductor solids with a band gap energy that is defined as the energy difference between the nonconductive and the conductive state of the material. The band gap energy can be also defined as the energy difference between the top of the valence band and the bottom of the conduction band. The photo-excitation of the solid occurs when light of suitable energy (higher than the value of the bandgap energy) induces the separation of electron and hole pairs by migration of electrons from the valence to the conduction band:

Photocatalyst



The photo-produced electrons and holes can give rise to reduction and oxidation reactions,

respectively, with adsorbed reacting species (Voïnov and Augustynski 1997).

The semiconductor photocatalyst is more frequently used both as powders (micro- or nanocrystalline samples) and films is bare polycrystalline TiO_2 in the anatase phase (Augugliaro et al. 2010) but also the other polymorphic rutile and brookite phases have been used. Moreover, the formation of nanorods, nanotubes, and nanowires under particular experimental conditions has been reported (Augugliaro et al. 2010). TiO_2 can be also doped with various transitional or rare earth metal species and non-metal species of N, C, S, and F. Sensitization with (metal) phthalocyanines and porphyrins to extend the light absorption in the visible region and/or to increase the lifetime of the photo-produced electron-hole pairs has been also proposed (Wang et al. 2010). Metallization with Pt or other noble metals has proved to be beneficial to induce some photo-reduction reactions, as for instance H_2 production from H_2O (Chiarello et al. 2011). Other oxides as for instance ZnO , WO_3 , MoO_3 , Fe_2O_3 , ZrO_2 , sulfides as ZnS , CdS , MoS_2 , or polyoxometalates as the heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ have been also successfully tested as photocatalysts (Di Paola et al. 2012). They have been also mixed with or supported on SiO_2 or Al_2O_3 with the aim to increase the surface area and to have the possibility to improve adsorption of the reacting species before their chemical transformation on photoactive sites of adjacent particles of the semiconductor photocatalyst. They have been also used in combination with membranes forming devices called “photocatalytic membrane reactors” (Molinari et al. 2010).

Some photocatalysts are not (photo)stable in liquid-solid systems, especially in aqueous environments and the extent of this instability strongly depends on the pH conditions. For instance, (i) anodic photocorrosion is observed for ZnO and various sulfides and (ii) the recovery of polyoxometalates from the reacting medium is problematic, due to their high solubility. The above phenomena generally are not observed when the photoreactions are carried out in gas-solid systems, although in the latter system deactivation of photocatalyst has been sometimes

observed, depending on the type of reagent molecules and on the experimental conditions used, as for instance the presence of water vapor.

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- chemical interactions without the occurrence of a permanent modification of its chemical composition. After each cycle of interaction between the reagent(s) and the photocatalyst, the chemical composition of the last is regenerated. The presence of a photocatalyst gives rise to an enhancement of the rate of a chemical reaction or its initiation under ultraviolet, infrared, or visible light illumination and the role of light is to photoexcite the solid that works as the photocatalyst (Braslavsky et al. 2011). The membrane has the task to immobilize the photocatalyst and to act as a molecular separation barrier for the reagents and/or reaction products (Molinari et al. 2002). A thin layer of a photocatalyst can be considered in principle a photocatalytic membrane, although the performance of some of them has not been reported.
- Some photocatalytic polysulfone membranes with the photocatalyst deposited and entrapped in the membrane were prepared and characterized by Molinari et al. (2002). It was found that adsorption of the pollutant on the membrane and membrane rejection play an important role in the global membrane performance showing interesting perspectives and synergy for coupling photocatalysis and membranes.
- Albu et al. (2007) showed a simple and robust fabrication process of a dense and free-standing membrane consisting of vertically oriented, both-side-open TiO₂ nanotubes. This membrane structure allows direct, size-selective, flow-through photocatalytic reactions with a very high efficiency.
- A semitransparent TiO₂ film with extraordinarily high photocatalytic activity was prepared by Sopyan et al. (1996) on a glass substrate by sintering a TiO₂ sol at 450 °C. Crystallographic analysis by X-ray diffraction and Raman spectroscopy showed that the film was purely anatase. The photocatalytic properties of the film were investigated by measuring the photodegradative oxidation of gaseous acetaldehyde at various concentrations under strong and weak UV light irradiation conditions. The photocatalytic activity of the film was higher than that of one of the most active commercial TiO₂ powders, Degussa P-25. The kinetics of acetaldehyde degradation as

Photocatalytic Membrane

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A photocatalytic membrane can be defined as a combination between a photocatalyst and a membrane. The photocatalyst is able to produce, by absorption of ultraviolet, infrared, or visible light, chemical transformations of reaction partners, repeatedly coming with them into various

catalyzed by the TiO₂ film as well as by P-25 powder were analyzed in terms of the Langmuir-Hinshelwood model.

TiO₂ and Ag-TiO₂ catalysts were supported in the form of thin layers by a dip-coating procedure on quartz substrate by Herrmann et al. (1997). The resulting materials were characterized by SEM/EDX, XRD, XPS, and UV-Vis absorption spectroscopy. The immobilized catalysts were tested in the photocatalytic degradation of malic acid and the increase of the photocatalytic activity can be explained by the enhanced electron-hole pair separation efficiency due to trapping of electrons by metallic Ag.

A novel chemistry method for the fabrication of robust nanostructured TiO₂ photocatalysts was developed by Choi et al. (2006). Such materials can be applied for developing efficient photocatalytic systems to be used for water treatment. The mesoporous photocatalytic TiO₂ membranes were synthesized via a simple method that involves dip-coating of appropriate substrates into an organic/inorganic sol composed of isopropanol, acetic acid, titanium tetraisopropoxide, and polyoxyethylene sorbitan monooleate surfactant (Tween 80) followed by calcination of the coating at 500 °C. Controlled hydrolysis and condensation reactions were achieved through in-taking of water molecules released from the esterification reaction of acetic acid with isopropanol. The subsequent stable incorporation of Ti-O-Ti network onto self-assembled surfactants resulted in TiO₂ photocatalysts with enhanced structural and catalytic properties. The properties included high surface area (147 m²/g) and porosity (46 %), narrow pore size distribution ranging from 2 to 8 nm, homogeneity without cracks and pinholes, active anatase crystal phase, and small crystallite size (9 nm). These TiO₂ photocatalysts were highly efficient for the destruction of methylene blue and creatinine in water. High water permeability and sharp polyethylene glycol retention of the prepared photocatalytic TiO₂/Al₂O₃ composite membranes evidenced the good structural properties of TiO₂ films. In addition, the multi-coating procedure enabled to control the physical properties of TiO₂ layer such as the coating thickness,

amount of TiO₂, photocatalytic activity, water permeability, and organic retention.

TiO₂ dispersed in polyester acrylate membranes was tested as a photocatalyst in the phenol mineralization reaction in the presence of O₂ by D'Arienzo et al. (2010). A kinetic study indicated that the embedded oxide maintains significant catalytic activity, and the result was first attributed to the homogeneous dispersion inside the polymeric host of TiO₂ nanocrystals. Furthermore, an investigation of the photogenerated charge carriers in the photocatalyst indicated that electrons are trapped on Ti³⁺ centers, while holes are trapped on C-centered species of the polymer matrix. In the presence of O₂, the C-centered radicals of the polymer transform into peroxy radicals, improving the charge separation in the polymer-embedded oxide with respect to the powder. The positive interference of the polymer matrix is responsible for the enhanced photoactivity of the embedded TiO₂.

Kim et al. (2003) proposed a hybrid thin-film-composite (TFC) membrane consisting of self-assembly of TiO₂ nanoparticles with photocatalytic destructive capability on microorganisms as a novel mean to reduce membrane biofouling. Microbial biofouling does not allow to realize high permeability over a prolonged period of reverse osmosis operation. The antifouling and fouling mitigation on the actual commercialized TFC was verified. TiO₂ anatase nanoparticles (≤10 nm) were prepared from the controlled hydrolysis of titanium tetraisopropoxide and characterized by X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM). TFC membrane was prepared by self-assembly of the TiO₂ nanoparticles through coordination and H-bonding interaction with the COOH functional group of aromatic polyamide thin-film layer. The hybrid membrane was shown to possess photobactericidal effect on *Escherichia coli* (*E. coli*) under UV light illumination. Introduction of TiO₂ nanoparticles on the actual commercial TFC membrane and application of reverse osmosis field test after exposure to microbial cells indicated the occurrence of a substantial prevention against the microbial fouling showing a less loss of reverse osmosis permeability.

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Photocatalytic Membrane Reactor

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A photocatalytic membrane reactor can be defined as a device existing in various configurations which combine a photocatalyst and a membrane to produce chemical transformations.

Some experimental results obtained by using various configurations of photocatalytic

membrane reactors (PMRs) have been discussed by Molinari et al. (2002). The configurations studied were (i) irradiation of the cell containing the membrane, with three sub-cases: (i(1)) catalyst deposited on the membrane; (i(2)) catalyst in suspension, confined by means of the membrane; (i(3)) entrapment of the photocatalyst in a PSF membrane; and (ii) irradiation of the recirculation tank and catalyst in suspension confined by means of the membrane. In the case of “(i),” a preliminary investigation of membrane stability under UV irradiation was carried out. PMR characterization in photodegradation tests was mainly carried out in a recycle batch membrane reactor and, in some cases, in a continuous membrane reactor. The comparison between the first set of results, where the membrane was used only as a support for the photocatalyst, and the newest ones, where the adsorption of the pollutant on the membrane and membrane rejection play an important role in the global reactor performance, showed interesting perspectives and synergy for coupling photocatalysis and membranes. Furthermore, the configuration where the recirculation tank was irradiated and the catalyst was used in suspension appeared to be the most interesting for industrial applications. For example, in reactor optimization, high irradiation efficiency, high membrane permeate flow rate, and selectivity can be obtained by sizing separately the “photocatalytic system” and the “membrane system” and taking advantage of all the best research results for each system.

A photocatalytic membrane reactor was tested for degradation of toxic organic species dissolved in water (Molinari et al. 2000). The catalyst, TiO_2 P25 Degussa, was immobilized by means of a flat sheet polymeric membrane and 4-nitrophenol (4-NP) was used as a model molecule to evaluate the reactor performance. A preliminary investigation of the stability, under UV irradiation, of some eligible polymeric membranes was carried out by using scanning electron microscopy (SEM), optical microscopy (OM), determinations of water permeation flux (WPF), and total organic carbon (TOC). These tests showed that commercial membranes made of fluoride + PP (FS 50 PP-Dow), polysulfone + PP (GR 51 PP-TechSep), and polyacrylonitrile (PAN-TechSep) seemed to be quite

stable to UV light over a 24 h period of irradiation. Immobilization of TiO_2 onto membranes by ultrafiltrating TiO_2 suspensions showed an optimal layer density slightly >2.04 mg TiO_2 per square cm of membrane surface area. Results obtained from membrane reactor studies indicated that the observed initial rate constants for the degradation of 4-NP were almost independent on the amount of TiO_2 employed over the range $0.76\text{--}4.08$ mg/cm². A 50 % weight degradation of 4-NP after 5 h of irradiation in the presence of air was obtained. Instead, an almost complete degradation of 4-NP was observed in the presence of TiO_2 suspended in the solution and pure oxygen. The permeate deriving from the membrane photoreactor was clear, and 4-NP concentration was approximately equal to that found in the retentate. The possibility of the continuous reuse of the photocatalyst and the continuous separation of products from the reaction medium gives some advantages over traditional approaches.

The ability of cross-flow ultrafiltration (UF) combined with photocatalytic reactions to separate TiO_2 photocatalysts from treated water in photocatalytic drinking water treatment was studied by Lee et al. (2001). The effect of natural organic matter (i.e., humic acids) and cross-flow velocities on UF fluxes and organic removal was explored with and without UV irradiation in the photocatalytic reactor. The interaction between the two solutes in the system, humic acids and TiO_2 photocatalysts, played a significant role in the formation of dense cake layers at the membrane surface, leading to a greater flux decline during ultrafiltration of TiO_2 particles. According to visual observations of the used membranes and the estimation of back-transport velocities of the solutes, a substantial amount of TiO_2 deposited on the membrane induces more humic acids to accumulate at the membrane through the adsorption of humic acids onto TiO_2 particles. The humic acid-laden TiO_2 particles offered more than four times higher specific cake resistance with a substantially increased compressibility coefficient than TiO_2 particles alone. The higher the cross-flow velocities, the greater the UV254 removal achieved. This was because the rise of cross-flow velocities contributed to the reduction of concentration

polarization at the membrane surface, thereby resulting in a decrease of the driving force for humic acids to pass through the membrane. When photocatalytic reactions took place with UV illumination, UV254 removal efficiencies of the permeate were improved markedly, and also the permeate flux was kept at a constant level without any sign of fouling. Although humic acids were not completely mineralized by photocatalysis, the degradation of the humic acids helped to enhance the UF flux, as they were transformed into less absorbable compounds.

The photodegradation of different pharmaceuticals [furosemide, ranitidine (hydrochloride), ofloxacin, phenazone, naproxen, carbamazepine, and clofibric acid] in aqueous medium at various pHs by using a batch photoreactor and a photocatalytic membrane reactor working in recirculation regime was carried out by Molinari et al. (2006). Polycrystalline TiO_2 was used as the photocatalyst, and different membranes (NTR 7410, PAN GKSS HV3/T, N 30 F, NF PES 10) were tested. A different adsorption of the substrates onto the catalyst surface was observed owing to the hydrophilic/hydrophobic character of the catalyst, depending on the pH. The photodegradation of the seven molecules in the batch reactor was successfully carried out, and the behavior was in accordance with pseudo-first-order kinetics. Furosemide and ranitidine were selected to carry out the study of rejection and photodegradation in the hybrid membrane system. The permeate flux of the treated water was in the $31.5\text{--}60.0$ L/(h m²) range for NTR 7410 membrane, whereas rejection values in the range 10–60 % for furosemide and 5–30 % for ranitidine in the dark (without photoreaction) were found. The degradation in the hybrid membrane photoreactor showed that the photocatalyst was retained by the membrane in the reaction ambient, while the membrane rejection toward the pollutants was not very satisfactory. A net decrease of the rejection down to 0 was observed in the contemporary presence of light, photocatalyst, and oxygen.

A batch-recirculated photoreactor was combined with a hollow fiber membrane ultrafiltration (UF) unit for heterogeneous photocatalysis applications (Sopajaree et al. 1999). The operation and

modeling of the UF process component and the performance of the integrated photoreactor-UF process assembly were studied. Methylene blue and titanium dioxide (Degussa P-25) were used as the test pollutant and photocatalyst, respectively. The influence of cross-flow velocity, transmembrane pressure, and TiO_2 dose on the permeate flux through the hollow fiber membrane was described. These data are modeled on the basis of concentration polarization and gel layer formation at the membrane surface/feed slurry boundary. The operation of the integrated photoreactor-UF assembly over ten repeated cycles was experimented. Photocatalyst separation was complete as gauged by nephelometric turbidity measurements. However, a systematic degradation in the photocatalyst performance was noted with each repeated cycle. Dynamic laser light-scattering data were consistent with agglomeration of the TiO_2 particles as a result of the UF process and suggest a possible factor in the degraded photocatalytic activity.

A photocatalytic reactor membrane pilot system, employing UV/ TiO_2 photocatalysis, was evaluated by Benotti et al. (2009) for its ability to remove 32 pharmaceuticals, endocrine-disrupting compounds, and estrogenic activity from water. Twenty-nine of the targeted compounds in addition to total estrogenic activity were greater than 70 % removed, while only three compounds were less than 50 % removed following the highest level of treatment (4.24 kWh/m^3). No estrogenically active transformation products were formed during treatment. Additionally, the unit was operated in photolytic mode (UV only) and photolytic plus H_2O_2 mode (UV/ H_2O_2) to determine the relative amount of energy required. Based on the electrical energy per order (EEO), the unit achieved the greatest efficiency when operated in photolytic plus H_2O_2 mode for the conditions tested.

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Photocatalytic Membrane Reactor: Conversion of Organic Compounds

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Photocatalytic synthesis in membrane reactors is still at a preliminary research stage, despite the great potentiality of photocatalytic processes, especially when they are coupled with a membrane separation system.

The possibility of using a membrane photoreactor for organic synthesis, developing a hybrid system in which the photocatalytic reaction and the separation of the desired product occurs in one step is of high interest.

Some results obtained in a photocatalytic membrane contactor (PMC) for the one-step synthesis of phenol, and its simultaneous separation, are reported by Molinari et al. (2009). TiO_2 has been used as catalyst, benzene as both reactant and extraction solvent, and a polypropylene

membrane to separate the organic phase from the aqueous reactive environment. To avoid secondary products and to obtain an efficient phenol production, the use of a membrane system, with high phenol permeability and complete rejection of the catalyst, coupled with the photocatalytic process, seems a useful solution. The membrane photoreactor built in this study consists of an external lamp placed on a batch reactor containing the aqueous solution with the catalyst in suspension; by means of a peristaltic pump, the solution is withdrawn from the photocatalytic reactor to a membrane contactor module in which a benzene solution is present as strip phase.

A set of preliminary experiments were performed in order to select the operating conditions to be employed in the batch and membrane systems. Due to the low solubility of benzene in water and to its high volatility, it was necessary to work with an excess of substrate in solution. By comparing the data in batch experiments obtained at pH values equal to 5.5 and 3.1, it was observed that the more acidic pH condition allowed to obtain a slightly increase of phenol production in the aqueous phase and a constant flux in the organic phase after 2 h (1.27 mmol/hm^2). Moreover, the area of the three main HPLC peaks detected at retention times of 3.0, 3.6, and 3.9 min indicated that a lower formation and extraction of these intermediates occurred at the acidic pH.

Other works concerning photocatalytic conversions are reported in the following. Selective oxidation of various primary and secondary alcohols was studied by Pillai and Sahle-Demessie (2002) in a gas phase photochemical reactor using immobilized TiO_2 catalyst. An annular photoreactor was used at 463 K with an average contact time of 32 s. The system was found to be specifically suited for the selective oxidation of primary and secondary aliphatic alcohols to their corresponding carbonyl compounds. Benzylic alcohols gave higher conversions, however, with more secondary reaction products. The reaction mechanism for various products formed was explained. The effects of different reaction parameters, such as O_2 /alcohol ratio, water vapor, UV light, and contact time, were studied. The

presence of oxygen was found to be critical for the photooxidation. Water vapor in the feed was also found to be beneficial, although it was not as critical as in hydrocarbon oxidation, where it was necessary for hydroxylating the catalyst surface and sustaining its activity. In alcohol oxidation, surface hydroxylation could be partially provided by the hydroxyl groups of the alcohol itself. Catalyst deactivation was also observed and it was attributed to the surface accumulation of reaction products. However, the catalyst regained its original activity after regeneration by calcination in air for 3 h at 723 K.

Selective photocatalytic oxygenation of various substrates was achieved using organic photocatalysts via photoinduced electron transfer reactions of photocatalysts with substrates and dioxygen under visible light irradiation (Fukuzumi and Ohkubo 2013). Photoinduced electron transfer from benzene to the singlet excited state of the 3-cyano-1-methylquinolinium ion enabled the oxidation of benzene by dioxygen with water to yield phenol selectively. Alkoxybenzenes were obtained when water was replaced by alcohols under otherwise the same experimental conditions. Photocatalytic selective oxygenation reactions of aromatic compounds was also achieved using an electron donor-acceptor, 9-mesityl-10-methylacridinium ion acting as a photocatalyst, and dioxygen as an oxidant under visible light irradiation.

The most recent advances in the application of heterogeneous photocatalysis to synthesize valuable compounds by selective oxidation and reduction are reported by Palmisano et al. (2010).

The photocatalytic oxidation of 4-methoxybenzyl alcohol in water was performed in a fixed bed continuous annular reactor by using a home-prepared TiO_2 catalyst supported on Pyrex glass beads (Yurdakal et al. 2010). The investigation was aimed to modeling the complex kinetics of the photoprocess which occurs through two parallel pathways: (i) partial oxidation to the corresponding aldehyde and (ii) total oxidation to CO_2 and H_2O . On these grounds, the influence of liquid flow rate, inlet concentrations of alcohol and oxygen, catalyst amount, and irradiation power on the photoreactivity were studied.

A kinetic model like that of Langmuir-Hinshelwood satisfactorily fitted the experimental results and allowed determination of the values of model parameters. It was found that all these parameters are positively affected by an increase of radiant energy absorbed by the catalyst. All the reactivity results indicate that the partial oxidation pathway is favored by the low flux of absorbed photons and by low oxygen coverage on the TiO₂ surface; opposite conditions favor the mineralization pathway.

The photoproduction of vanillin was studied in aqueous medium starting from *trans*-ferulic acid, isoeugenol, eugenol, or vanillyl alcohol by using both commercial and home-prepared TiO₂ samples as photocatalysts (Augugliaro et al. 2012). The visible light-induced oxidation of *trans*-ferulic acid by TiO₂ photocatalysis was also carried out under visible light via the formation of a charge-transfer complex (Parrino et al. 2012). A drawback for this type of photoreaction is the relatively low selectivity observed and the presence of other products. The combination of photocatalysis and pervaporation by using nonporous membranes has been suggested to separate the vanillin or other aldehydes from the irradiated suspension to avoid their subsequent oxidation, increasing in such a way the selectivity (Camera Roda et al. 2010; Camera Roda et al. 2013). The mild experimental conditions used suggest that heterogeneous photocatalysis could be in some cases an alternative green route for replacing environmentally hazardous processes with safe and energy efficient routes.

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Photocatalytic Membrane Reactor: Degradation of Organic Compounds

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Degradation of organic compounds in photocatalytic membrane reactors has been one of the first applications in the combination of photocatalysis and membranes. The possibility of using a membrane photoreactor for degradation of organics, developing a hybrid system in which the photocatalytic reaction and the separation of the desired product occur in only one device, is of high interest. Some results obtained in this application are reported in the following.

The ability of cross-flow ultrafiltration (UF), combined with photocatalytic reactions, to separate TiO₂ photocatalysts from treated water in photocatalytic drinking water treatment was investigated by Lee et al. (2001). The effect of natural organic matter (i.e., humic acids) and

cross-flow velocities on UF fluxes and organic removal was explored with and without UV irradiation in the photocatalytic reactor. The interaction between the two solutes in the system, humic acids and TiO_2 photocatalysts, played a significant role in the formation of dense cake layers at the membrane surface, leading to a greater flux decline during ultrafiltration of TiO_2 particles. According to visual observations of the used membranes and the estimation of back-transport velocities of the solutes, a substantial amount of TiO_2 deposited on the membrane induced a higher amount of humic acids to accumulate at the membrane through the adsorption onto TiO_2 particles. The humic-acid-laden TiO_2 particles offered more than four times higher specific cake resistance with a substantially increased compressibility coefficient than TiO_2 particles alone. The higher the cross-flow velocities, the greater the UV254 removal achieved. This was because the rise of cross-flow velocities contributed to the reduction of concentration polarization at the membrane surface, thereby resulting in a decrease of the driving force for humic acids to pass through the membrane. When photocatalytic reactions took place with UV illumination, UV254 removal efficiencies of the permeate were improved markedly, and also the permeate flux was kept at a constant level without any sign of fouling. Although humic acids were not completely mineralized by photocatalysis, the degradation of the humic acids helped to enhance the UF flux, as they were transformed to less adsorbable compounds.

A photocatalytic reaction system, composed of solution and gas spaces divided by a thin Teflon film and TiO_2 -coated mesh or cloth, for the treatment of contaminated aqueous solutions was developed to be operated with enhanced aeration without bubbling of air in the solution (Villacres et al. 2003). First, the photocatalytic activities of TiO_2 particles immobilized on two kinds of support material, stainless steel mesh (SSM) and fiberglass cloth (FGC), were investigated for photocatalytic oxidation of 2-propanol, as a model volatile organic compound, dissolved in aerated aqueous solution. The TiO_2 particles immobilized on both support materials exhibited photocatalytic activity to oxidize 2-propanol into

acetone and carbon dioxide (CO_2), and the activity levels of the TiO_2 particles immobilized on the two kinds of support materials were comparable. Presumably due to the presence of a small amount of metal species originating in SSM that might work as reduction catalysts, molecular hydrogen H_2 was also liberated on the TiO_2 -immobilized SSM. Results of analysis of weight loss after photoirradiation suggested that the stability of the TiO_2 -immobilized FGC was better than that of the TiO_2 -immobilized SSM. On the basis of these results, FGC was employed in construction of a photocatalytic reactor equipped with an O_2 -permeable Teflon membrane in order to make oxygen pass from a gas space to a solution space and to keep the surface of the immobilized TiO_2 photocatalyst, facing an aqueous solution containing volatile organic compounds, saturated with dissolved O_2 . From the results of photocatalytic oxidative decomposition of 2-propanol, it was clarified that the surfaces of TiO_2 particles could be sufficiently supplied with O_2 from the gas space through the membrane to accelerate the oxidation.

Dyes are organic compounds used in textile, food, and drug industries, and their abatement represents one of the main problems in the treatment processes because generally they are very stable toxic compounds. Two commercial azo-dyes, i.e., Congo Red ($\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$) and Patent Blue ($\text{C}_{27}\text{H}_{31}\text{N}_2\text{NaO}_6\text{S}_2$), in aqueous solution were degraded in a photocatalytic membrane reactor (Molinari et al. 2004) by using TiO_2 Degussa P25 as the catalyst. Different system configurations and irradiating sources were studied, and the influence of some operational parameters such as the pressure in the membrane cell and the initial concentration of the substrates were determined. A comparison between suspended and entrapped TiO_2 was also done. The experimental results showed a satisfactory degradation efficiency of the photocatalytic membrane process. The influence of various parameters (e.g., feed concentration, recirculation rate) has been discussed to obtain high reaction rates, operating stability, and high membrane rejection, both for substrates and by-products. Congo Red was photodegraded with higher rate under the same

experimental conditions probably due to its higher adsorption onto the catalyst surface. It was possible to treat successfully highly concentrated solutions (500 mg/L) of both dyes by means of a continuous process obtaining good values of permeate fluxes (30–70 L/m²h); this could be interesting for industrial applications. The reactor containing the suspended photocatalyst was significantly more efficient than the reactor containing the catalyst entrapped into the membrane.

An advanced oxidation process (AOP) with reactor capacity of 150 L, using ultraviolet (UV) radiation and TiO₂ photocatalyst, was evaluated for the destruction of toxic organic chemical, bisphenol A (BPA) by Thiruvengkatachari et al. (2005). TiO₂, in the form of powder, was suspended as slurry in the water avoiding the commonly adopted practice of immobilizing it onto a carrier material such as glass, concrete, or ceramics. Adsorption of BPA by TiO₂ was evaluated and was performed as a pretreatment to AOP. The combined effect of ozone with the AOP process was also studied. Coupling ozone with UV/TiO₂ brought about a synergistic effect on BPA degradation and 10 ppm of BPA, and the intermediate organic compounds were completely removed within 3 h. The highlight of this study was the simultaneous degradation of BPA and separation of TiO₂ particles from water after the photocatalytic treatment, in order to obtain reusable quality water. Separation of TiO₂ particles was carried out by a unique two-stage coagulation and settling process followed by submerged hollow fiber microfiltration membrane technique. With initial turbidity of 4,000 NTU, the turbidity of the final permeate water was well below 0.1 NTU. Some of the main advantages of this hybrid treatment system include the possibility of large-scale treatment, complete and efficient BPA and its organic intermediates degradation, easy separation and reuse of TiO₂ that resulted free from chemical coagulant contaminants, reusable quality water, and potentiality for continuous operation with simple process modifications.

A study of the photodegradation of different pharmaceuticals [furosemide, ranitidine (hydrochloride), ofloxacin, phenazone, naproxen,

carbamazepine, and clofibric acid] in aqueous medium at various pHs by using a batch photoreactor and a photocatalytic membrane reactor working in recirculation regime was carried out by Molinari et al. (2006). Polycrystalline TiO₂ was used as the photocatalyst, and different membranes (NTR 7410, PAN GKSS HV3/T, N 30F, NF PES 10) were tested. A different adsorption of the substrates onto the catalyst surface was observed owing to the hydrophilic/hydrophobic character of the catalyst, depending on the pH. The photodegradation of the seven molecules in the batch reactor was successfully carried out and the behavior was in accordance with pseudo-first-order kinetics. Furosemide and ranitidine were selected to carry out the study of rejection and photodegradation in the hybrid membrane system. The permeate flux of the treated water was in the 31.5–60.0 L/(h·m²) range for NTR 7410 membrane, whereas rejection values in the range 10–60 % for furosemide and 5–30 % for ranitidine in the dark (without photoreaction) were found. The degradation in the hybrid membrane photoreactor showed that the photocatalyst was retained by the membrane in the reaction ambient, while the membrane rejection toward the pollutants was not very satisfactory. A net decrease of the rejection down to 0 was observed in the contemporary presence of light, photocatalyst, and oxygen.

The combination of a dialysis membrane and a photocatalytic reactor into an original membrane photoreactor (MPR) to mineralize organic compounds contained in artificial turbid waters which were obtained by using natural clay named bentonite was studied by Azrague et al. (2007). Various systems have been described in the literature, combining photocatalysis with pressure-driven membrane techniques, such as nanofiltration (NF) and ultrafiltration (UF), but these systems can lead to membrane fouling. Only the combination of photocatalysis and membrane distillation avoids this problem, but it needs energy to reach pervaporation phenomena. The MPR system worked at ambient temperature, with the membrane used as a barrier for particles and to extract the organic compounds from the turbid water without transmembrane pressure. Thus it was

possible to separate the polluted turbid water from the photoreactor compartment and to separate TiO_2 continuously from the treated water. The photocatalytic reaction and dialysis were studied separately before the MPR process was developed. A model pollutant, 2,4-dihydroxybenzoic acid (2,4-DHBA), was mineralized from turbid waters by photocatalysis. By means of the membrane, the TiO_2 remained in the photoreactor compartment without filtration and bentonite was kept away from the photoreactor.

The degradation of toxic organic compounds such as trichloroethylene (TCE) in water, using a combined photocatalysis/microfiltration (MF) system, was focused by Choo et al. (2008). The performances of the hybrid system were investigated in terms of the removal efficiency of TCE and membrane permeability, in the presence or absence of humic acids and at different pHs. The fate of TCE during the photocatalytic reactions was checked in order to evaluate the feasibility of the photocatalytic membrane reactor (PMR). Greater TCE degradation (>60 %) was achieved with an increase in the TiO_2 dosage (up to 1.5 g/L) in PMR, but a substantially large TiO_2 dosage brought about a decrease in TCE degradation efficiency. The photocatalytic decomposition of TCE appeared to be more effective at acidic pH conditions than at a neutral or alkaline pH. The alkalinity and the addition of humic acids into the feedwater did not produce a significant effect on TCE degradation, while humic acids (whose dose was 1 mg/L as TOC) in the feedwater played a role in a decline of permeability by 60 %. Membrane permeability in the PMR was also affected by tangential velocities. An improvement of 60 % in flux was achieved when the tangential velocity increased from 0.19 to 1.45 m/s. This occurred because flow regimes can govern the deposition of TiO_2 particles on the membrane surface.

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Photocatalytic Membrane Reactors for Refractory Pollutants Degradation

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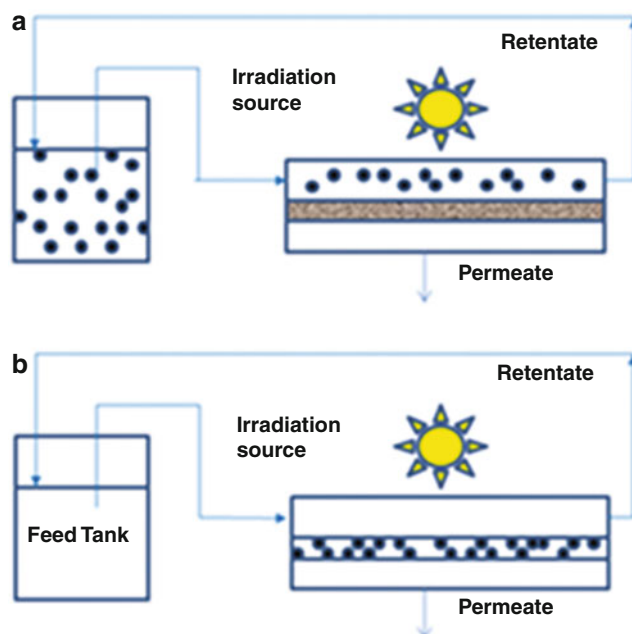
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The increasing emission of refractory organic pollutants has challenged the conventional water treatment. As one of the advanced treatment systems, photocatalytic oxidation has drawn significant attention in water treatment research because of its environmental compatibility and powerful oxidation ability. Photocatalysis is an acceleration of photoinduced reaction by the presence of a photocatalyst. Among the photocatalysts, titanium dioxide (TiO_2) has been proven to be an attractive and promising semiconductor catalyst in heterogeneous photocatalysis and in advanced oxidation

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Fig. 1 Main configurations of PMR, (a) photocatalyst in suspension and (b) photocatalyst coated on the membrane, inspired from Mozia (2010)



processes own to its unique photocatalytic efficiency. However, a main limitation remains: the separation of the catalyst from treated. Photocatalytic membrane reactor (PMR) with synthesized catalyst is thus a very promising method to overcome photocatalysis drawbacks (Mozia 2010). In such configuration, the membrane plays the role of a barrier for the photocatalyst and a selective barrier for the molecule to be degraded. The main advantage is to confine the photocatalyst in the reaction environment by means of the transmembrane flux, the control of the residence time of the molecule in the reactor, and the achievement of a continuous process with simultaneous catalyst and product separation from the reaction environment. It also allows some additional operations for catalyst recycling to be avoided, such as coagulation, flocculation, sedimentation, or filtration, and thus leads to energy saving and enables the size of the installation to be minimized. Finally, this configuration enables the main drawback of membrane processes to be overcome: the fact that it only transfers pollutant from a phase to another without treating it.

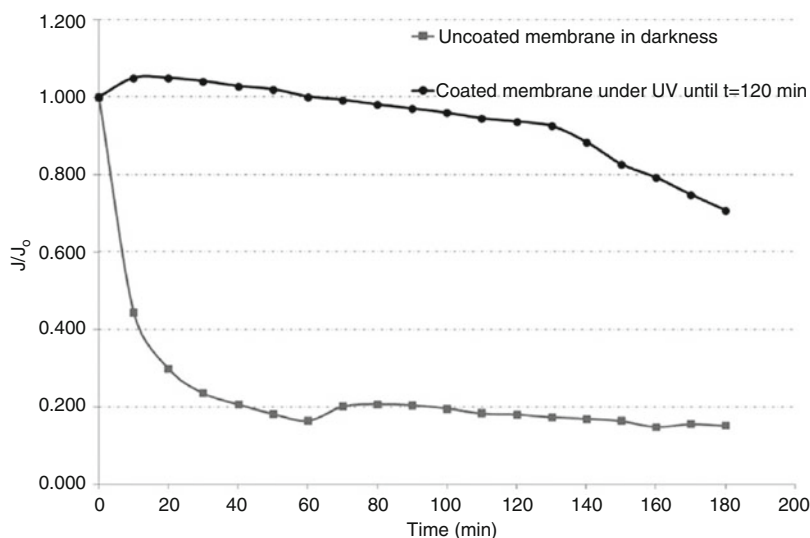
PMR can be divided into two main groups: photocatalyst in suspension or immobilized in/on

the membrane (Fig. 1). The major drawback of the first configuration (a) is the membrane fouling (leading to a decrease of the permeate flux) and the deterioration of the membrane surface when organic membranes are used. The second configuration (b) enables this drawback to be avoided as oxidation by hydroxyl radicals occurs on the external surface and within the pores of the membrane while reactants are permeating in a one pass flow. Main advantage of this configuration is to minimize mass transfer resistance between the bulk of the fluid and the semiconductor surface.

Concerning membrane with catalyst immobilized on the membrane surface, photoactive layer can be deposited using the dipcoating method followed by heat treatment: a membrane is dipped in a suspension of nanoparticles and then calcined (600 °C) to crystallize the TiO_2 (Mendret et al. 2013). For this, the use of ceramic membrane is less straightforward than polymeric membranes which can be more easily manipulated. In a PMR with TiO_2 immobilized, the membrane acts as a support for the catalyst and might act as a barrier for molecule present in the solution (initial compounds and products or by-products of their

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Fig. 2 Normalized permeate flow of uncoated and coated membranes during filtration of AO7 at 10 mg L^{-1} , pH = 6 (Figure from Mendret et al. 2013)



decomposition). The photodecomposition takes place on the membrane surface and thus membrane itself has to be irradiated. The main advantage is that membrane fouling could be reduced; thus permeate flux increased, because organic compounds which are responsible for fouling such as humic and fulvic acids are also decomposed as the surface of the membrane is reactive. Moreover, it was observed that deposition of titania on the membrane increases their hydrophilicity which contributes to fouling mitigation. Indeed, many studies have been conducted in the field of fouling mitigation of membranes (Gullinkala and Escobar 2010), and it is widely acknowledged that hydrophobic membrane surfaces have an obviously higher tendency to foul and to reduce permeability. Membrane surface properties such as hydrophilicity and charge determine the interaction between the membrane and the foulants. A hydrophilic membrane possesses a high surface tension and has the ability to form hydrogen bonds with water, and therefore a water layer exists between the membrane and the bulk solution which increases membrane hydrophilicity. As a consequence, such membranes are less prone to fouling. Moreover, it was experimentally put in evidence that TiO_2 layer under UV light enhances ceramic membrane wettability and enables higher and more stable flux to be reached rapidly (Fig. 2; Mendret et al. 2013).

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Photocatalytic Nanomaterials: Preparation and Properties

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Photocatalysis, in which solar photons are used to drive redox reactions to produce chemicals

on the surface of an irradiated semiconductor, is one of the main alternative solutions for renewable energy generation and environmental remediation.

In the category of photocatalytic materials, semiconductor materials have attracted considerable attention in the fields of solar energy conversion and environmental protection because it represents an easy way to utilize the energy of either natural sunlight or artificial indoor illumination. Of the many different photocatalysts, TiO_2 emerged in 1972 for the investigation of photonic energy conversion by photocatalytic method (Fujishima and Honda 1972). Since then, it has been the most widely studied and used in many applications because of its strong oxidizing abilities (Fujishima and Honda 1972; Nosaka et al. 2002, 2003a, b, 2004; Jańczyk et al. 2006; Fujishima et al. 2007) for the decomposition of organic pollutants, chemical stability, long durability, nontoxicity, low cost, and transparency to visible light.

Anatase- TiO_2 is well known as a semiconductor catalyst, which exhibits a better photocatalytic activity by irradiation of a light with energy greater than the band gap (3.2 eV) (Sopyan et al. 1994). The photocatalytic activity appears by irradiation of an ultraviolet (UV) light with wavelength shorter than 387 nm ($=3.2$ eV). The decomposition of harmful substances using the photocatalytic activity of anatase- TiO_2 has attracted a great deal of attention (Matsuda et al. 2000). This effect is attributed to the strong oxidant (hydroxyl radical), which generates at the surface of the TiO_2 crystals by the irradiation of UV light.

Doping of TiO_2 is one of the solutions to enhance/extend its photocatalytic properties. Utilizing Ag in conjunction with TiO_2 could potentially allow several different inactivation mechanisms to work in concert. Therefore, a synergism occurs between Ag and TiO_2 when Ag/ TiO_2 is used for inactivating microorganisms under UV radiation. Li et al. demonstrated, for example, that Ag-doping TiO_2 greatly enhanced the photocatalytic inactivation of viruses primarily by increasing $\text{HO}^\cdot$ production in addition to slightly increasing virus adsorption (Lig

et al. 2011). Wang et al. demonstrated that the deposition of Ag on the surface of TiO_2 would produce traps to capture the photoinduced electrons or holes, leading to the reduction of electron-hole recombination and thus improving the photocatalytic efficiency (Wang et al. 2008). The effect of Ag dopants on the lattice or surface of TiO_2 was also demonstrated to enable the catalyst to perform more effectively and shortens the illumination period (Lee and Hong 2005).

As demonstrated by Gleiter's group (Gleiter 1989), nanostructuring makes possible to design nanomaterials with enhanced properties or even generation of new functionalities which have not been obtained in conventional materials. This is the second solution to propose high-performance photocatalytic nanomaterials (Irie et al. 2009; Yashima et al. 2010; Liu et al. 2007). Small material size is generally beneficial for surface-dependent catalysis because it enhances specific surface area and also increased reactive sites. However, smaller material size is not always higher catalytic efficient because it can cause strong quantum confinement effect that increases the recombination probability of photogenerated electron-hole pairs (Chen et al. 2012; Song et al. 2013; Serpone et al. 2012). Therefore, photogenerated electron-hole pair migration requires a reduced recombination of suitable concentration gradient or potential gradient from the core to surface of materials that is correlated with morphology, structure, and surface properties of nanostructured materials.

Nowadays, because of their enhanced or even novel properties, photocatalytic nanomaterials have created more opportunities in extending the applications of photocatalytic materials in various fields such as water and air purifications, hydrogen generation, CO_2 reduction, dye-sensitized solar cells, antifogging surfaces, heat transfer and heat dissipation, anticorrosion, lithography, photochromism, solar chemicals production, and many others. They can be prepared using chemical routes such as sol-gel process and ammonia treatment of molecular precursors to exist in many compositions, in particular in oxide, oxynitride, and nitride systems.

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Photocatalytic Process

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A photocatalytic process is a set of reduction and oxidation photocatalytic reactions occurring in the presence of a photocatalyst (see photocatalyst) that gives rise to one or more products starting from organic or inorganic substrate(s).

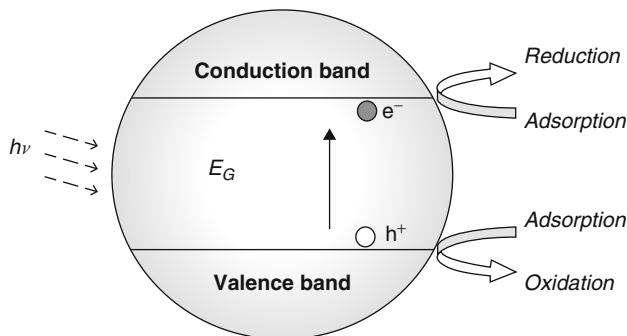
The distinction of the photocatalytic reactions in oxidation and reduction means that only the main product(s) derive(s) from oxidation or reduction,

respectively, of the main reagent(s). Noticeably, in fact, both the oxidative and reductive pathways are present in heterogeneous photocatalytic processes. Sometimes the reduction pathway produces species (e.g., $O_2^{\bullet-}$ by trapping electrons in the conduction band of a semiconductor photocatalyst) whose subsequent reaction (e.g., with H_2O) gives rise to $\bullet OH$ and $\bullet O_2H$ oxidant radicals.

The photoproducted holes can straightforwardly attack the adsorbed species or solvent molecules (for instance, H_2O) producing oxidant radical species. The following sketch represents the possible initial steps of a photocatalytic process (Fig. 1).

The heterogeneous photocatalytic oxidations are generally unselective, and several studies and applications have been reported, for instance, in the field of outdoor and indoor environment purifications to abate low concentrations of organic and inorganic pollutants (Serpone and Emeline 2005). The heterogeneous photocatalytic method appears to be efficient only in those cases where low concentrations of pollutants are present because the presence of high concentrations slows down the reaction rates. Moreover, it should be checked, with great care, both the absence of mass transfer phenomena controlling the reaction kinetics and the possible photocatalyst deactivation, due to possible accumulation of by-products and/or intermediates onto the photocatalyst surface which could block the (photo)active sites (particularly for long lasting runs in gas-solid systems). These problems are not dramatic in the aqueous systems. A moderate mixing of the reacting suspension is sufficient to guarantee the absence of a mass control on the reaction kinetics. The photocatalyst surface, in fact, is cleaned by production of a high number of oxidant radicals that induce consecutive attacks to the intermediates giving rise to their complete mineralization by means of several adsorption-desorption steps. In addition, the mineralization can proceed through intermediates that do not desorb into the bulk of solution, but are subjected to oxidant attacks onto the surface until the formation of CO_2 . Indirect evidence of this behavior in many cases is the detection of CO_2 soon after the starting of irradiation.

Heterogeneous photocatalytic processes have been more recently addressed also toward the

Photocatalytic Process,**Fig. 1** Photocatalytic Process

selective production of high-value molecules in mild experimental conditions by using suitable photocatalysts, solvent and starting substrates (Palmisano et al. 2010; Augugliaro and Palmisano 2010), and, in some cases, also membranes (Molinari et al. 2009).

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Photocatalytic Processes by Membrane Operations

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A photocatalytic process combined with membrane operations is a set of reduction and

oxidation photocatalytic reactions occurring in the presence of a photocatalyst (see “► Photocatalytic Process”) and a membrane giving rise to one or more products (see “► Photocatalytic Membrane Reactor”) starting from organic or inorganic substrate(s).

Photocatalysis and, in particular, heterogeneous photocatalysis is a process of great potentiality for pollutants abatement. To improve the overall performance of the photoprocess, heterogeneous photocatalysis has been often combined with physical or chemical operations, which affect the chemical kinetics and/or the overall efficiency. Various possibilities to couple heterogeneous photocatalysis with other technologies to photodegrade organic and inorganic pollutants dissolved in actual or synthetic aqueous effluents have been described by Augugliaro et al. (2006). These combinations increase the photoprocess efficiency by decreasing the reaction time with respect to the separated operations or they decrease the cost with respect to heterogeneous photocatalysis alone, generally in terms of light energy. Depending on the operation coupled with heterogeneous photocatalysis, two categories of combinations exist. When the coupling is with ultrasonic irradiation, photo-Fenton reaction, ozonation, or electrochemical treatment, the combination affects the photocatalytic mechanisms thus improving the efficiency of the photocatalytic process. When the coupling is with biological treatment, membrane reactor, membrane photoreactor, or physical adsorption, the combination does not affect the photocatalytic mechanisms, but it improves the efficiency of the overall process. The choice of the coupling is related to the type of wastewater to be

treated. A synergistic effect, giving rise to an improvement of the efficiency of the photocatalytic process, has been reported in the literature for many cases.

The influence of the type of nanofiltration membrane, initial concentration of pollutant, and pH on the photodegradation rate was investigated by Molinari et al. (2002) in discontinuous and continuous configurations in a photocatalytic membrane system with the lamp immersed in the suspension inside the photoreactor by using polycrystalline TiO_2 (Degussa P25) as the catalyst and humic acids, organic dyes, and 4-nitrophenol as the pollutants. Two membranes were tested, i.e., NF-PES-010 (Celgard, Germany) of polyethersulfone and NTR-7410 (Nitto Denko, Japan) of sulfonated polyethersulfone. The last one was chosen for all of the photoreactivity experiments because permeability and rejection tests indicated that it was able to hold both catalyst and small molecules carrying the same membrane charge (negative), thanks to the Donnan exclusion. Despite the fluxes ranged between 20 and 40 $\text{L h}^{-1} \text{m}^{-2}$ in operating conditions at 6 bar and these values were interesting for application purposes, the rejections of NTR-7410 nanofiltration membrane, obtained during operation of the membrane photoreactor in the degradation of humic acids, patent blue dye, and 4-nitrophenol, were significantly lower than those obtained in the absence of photodegradation, probably because of the small molecular size of the by-products and of the intermediate species produced during the photodegradation process. This means that in order to select a suitable membrane, rejection should be determined during operation of the photoreactor.

A batch-recirculated photoreactor was combined with a hollow-fiber membrane ultrafiltration (UF) unit for heterogeneous photocatalysis applications. The operation and modeling of the UF process on the performance of the integrated photoreactor-UF process was studied by Sopajaree et al. (1999). Methylene blue and titanium dioxide (Degussa P-25) were used as the test pollutant and photocatalyst, respectively. The influence of cross-flow velocity, transmembrane pressure, and TiO_2 dose on the permeate flux through the hollow-fiber membrane was described. The data were modeled

on the basis of concentration polarization and gel layer formation at the membrane surface/feed slurry boundary.

The photocatalytic degradation of natural organic matter (NOM) is an attractive option in the treatment of drinking water (Choo et al. 2008). The performance of a submerged photocatalytic membrane reactor (PMR) was investigated with regard to the removal of NOM and the control of membrane fouling.

The efficiency of a hybrid system combining photocatalysis and membrane filtration in a single module was investigated. Low-pressure submerged hollow-fiber membranes were used to retain the TiO_2 particles in the system by Chin et al. (2007) during the photodegradation of bisphenol A (BPA) as the model pollutant. Aeration was applied in the submerged membrane photoreactor (SMPR) to provide (i) mixing, (ii) dissolved oxygen, (iii) mechanical agitation (to prevent agglomeration of TiO_2 particles), and (iv) shear forces (to remove TiO_2 particles from the membrane surface). It was found that intermittent permeation enhanced the sustainability of the submerged membranes but showed no effect on the photoactivity of the system. An intermittence aeration frequency (IF) of 0.1 was sufficient to reduce the fouling rate of the membrane under the experimental conditions. The SMPR appears to be very effective and can achieve removal of low-concentration organics (such as BPA) in a compact, low-energy system. The combined photocatalytic and membrane processes have been more recently addressed also toward the selective production of high-value molecules in mild experimental conditions by using suitable photocatalysts, solvent, and starting substrates and membranes (Molinari et al. 2009a, b; Augugliaro and Palmisano 2010).

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Photodegradation

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Photodegradation concerns the breaking of a molecule to smaller molecules (degradation and/or mineralization) by means of the absorption of photons of suitable wavelength such as that found in the infrared radiation, visible light, and ultraviolet light of the solar spectrum. Photodegradation also includes the change of the shape of a molecule such as protein denaturation and the addition of other atoms or molecules. One type of photodegradation reaction is oxidation which is used to purify some drinking water and wastewater to destroy pollutants. Photodegradation can be photochemical and photocatalytic: in the first case only light is used, while in the second case a combination of light

and a semiconductor photocatalyst is used. In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalysts (e.g., TiO_2 and ZnO), an energetic light source, and an oxidizing agent such as oxygen or air. Photocatalytic degradation in aqueous medium is mainly dependent on the solution pH, catalysts and their composition, organic substrate type (usually pollutants) and concentration, light intensity, catalyst loading, ionic composition of wastewater, types of solvent, oxidant concentration, and calcination temperatures of the photocatalyst (Ahmed et al. 2010).

In the degradation of organic pollutants, various compounds such as dyes (Molinari et al. 2003), drugs (Molinari et al. 2006), pesticide and herbicide derivatives dominant in storm water, and wastewater effluent have been treated. In the photocatalytic process, the hydroxyl radical, which is generated from the oxidation of adsorbed water as $\text{OH}^\cdot$, is the primary oxidant species, while the presence of oxygen prevents an electron-hole pair recombination. In the photocatalytic degradation of pollutants, when the reduction process of oxygen and the oxidation of pollutants do not proceed simultaneously, there is an electron accumulation in the CB, thereby causing an increase in the rate of recombination of e^- and h^+ . Thus it is of paramount importance to prevent electron accumulation in efficient photocatalytic oxidation. In photocatalysis, TiO_2 has been studied extensively because of its high activity, desirable physical and chemical properties, low cost, and availability. Among the TiO_2 crystalline forms, anatase and rutile forms have been investigated extensively as photocatalysts. Anatase has been reported to be more active as a photocatalyst than rutile.

Heterogeneous photocatalysis involving zinc oxide (ZnO) emerges as a promising new route for water purification process in terms of the degradation and mineralization of dyes discharged into wastewater from textile and other industrial processes (Lam et al. 2012), although ZnO can give rise to anodic photocorrosion in aqueous systems, depending on the experimental conditions chosen.

Removal of nitrogen-containing organic compounds in wastewater by TiO_2 photocatalytic degradation is the result of a strong interaction among pollutant structures, TiO_2 properties, and photocatalytic reaction conditions. It is also clear that for each organic pollutant, a unique set of conditions may be needed for the optimal performance (Jing et al. 2011).

Solid-phase photocatalytic degradation for eco-friendly disposal of polymer such as waste plastics has been also studied. Composite plastics embedding photocatalysts into polymer matrix have excellent photocatalytic degradation activity. They could be degraded effectively in ambient air under sunlight exposure (Yang et al. 2011).

Photoelectrochemical cell and the factors that affect efficient production of electricity and hydrogen by photocatalytic degradation of (principally) organic and (secondarily) inorganic waste materials are reported by Lianos. Materials used for making a photoanode and the rest of the components of the cell as well as the models of cell efficiency and photodegradation procedures during cell operation have been also described (Lianos 2011).

Efficient photochemical systems for environmental remediation can be constituted by a semiconductor and a surface-adsorbed antenna molecule (dyes or other color species). The major advantage of these systems is that they are able to achieve the degradation of organic pollutants by using visible light from the sun as energy and O_2 in the air as the oxidant under ambient conditions (Chen et al. 2010).

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Photolysis in Photocatalytic Membrane Reactors

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Photolysis is a chemical process which is able to break down molecules into smaller units through the absorption of light. It can be carried out in a device combining also a membrane. Some results obtained in various photocatalytic membrane reactors are summarized in the following.

Some advanced oxidation processes (AOPs) such as Fenton $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, photo-assisted Fenton $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$, UV photolysis, and photo-assisted Fenton like $\text{UV}/\text{O}_2/\text{Fe}^{2+}$ have been tested for the degradation of gemfibrozil (a widely used blood lipid and cholesterol-modifying drug) in aqueous solution in a batch system and then in a membrane reactor (Molinari et al. 2007). A nanofiltration/reverse osmosis type cross-linked polyamide UTC-60 (Toray) membrane (19 cm^2) was used. Gemfibrozil at an initial concentration equal to 5 mg/L was degraded in the batch degradation tests by employing the four

AOPs, but numerous peaks of intermediates were observed by HPLC analyses. Indeed dissolved oxygen concentration (DOC) analyses indicated a poor mineralization in the case of photolysis (3.1 %) and UV/O₂/Fe (10 %), whereas values of 62 % and 24 % were obtained by using photo-assisted Fenton and Fenton AOPs, respectively. Thus, in the membrane reactor, only the Fenton and the photo-assisted Fenton were tested. In the latter case the results showed a drug degradation higher than 92 %, a mineralization higher than 55 %, and a membrane retention of the catalyst in solution higher than 95 %.

The combination of a dialysis membrane and a photochemical reactor into a membrane photoreactor (MPR) to mineralize organic compounds was described by Azrague et al. (2005). A pollutant model (2,4-dihydroxy benzoic acid) was mineralized from turbid waters in the photoreactor by using VUV (vacuum ultraviolet) irradiation (172 nm). A model based on diffusion through the membrane and first-order reaction in the reactor was in good agreement with the experimental data, in a wide range of operating conditions. This “advanced oxidation process” produces high concentrations of hydroxyl radicals and is a good method to mineralize organic compounds.

The membrane efficiency to photodegrade typical water pollutants was evaluated in a continuous flow water purification device, applying UV irradiation on both membrane sides by Romanos et al. (2012). The developed composite NF membranes were highly efficient in the decomposition of methyl orange exhibiting low adsorption-fouling tendency and high water permeability. A chemical vapor deposition (CVD)-based innovative approach was applied with the purpose to develop composite TiO₂ photocatalytic nanofiltration (NF) membranes. The method involved pyrolytic decomposition of titanium tetrakisopropoxide (TTIP) vapor and formation of TiO₂ nanoparticles through homogeneous gas-phase reactions and aggregation of the produced intermediate species. The grown nanoparticles are diffused and deposited on the surface of gamma-alumina NF membrane tubes. The CVD reactor allowed for online monitoring

of the carrier gas permeability during the treatment, providing a first insight on the pore efficiency and thickness of the formed photocatalytic layers. In addition the thin TiO₂ deposits were developed on both membrane sides without sacrificing the high yield rates. Important innovation was also introduced in what concerns the photocatalytic performance evaluation.

Fulvic acids were removed from model solutions by catalysis, photolysis, and photocatalysis, as well as in the integrated process of photocatalysis and ultrafiltration (Rajca et al. 2011). Experiments were carried out in the Heraeus reactor, where model water of an approximately 10 g/m³ content of fulvic acids was treated. TiO₂ was used as a photocatalyst. The efficiency of fulvic acid oxidation, measured in terms of dissolved organic carbon content and UV absorbance ($\lambda = 254$ nm), was related to the pH of the water (3.5, 7.0 and 10.0) and to the catalyst dose applied (100–600 gTiO₂/m³). The results indicated the efficiency of the photocatalytic process for fulvic acid removal from water and the usefulness of the ultrafiltration membrane in the recovery of the catalyst used. The values of the reaction rate constant and the halftime of fulvic acid degradation were determined using a kinetic model based on a first-order reaction. Relations between rate constant, pH, and photocatalyst concentration in the reaction environment were found.

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Photooxygenation

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The combination of molecular oxygen (also from air) and light for carrying out chemical conversions is named photo-oxygenation. In the following some applications of this method, involving also membranes, are described.

Synthesis of a series of porphyrin-functionalized pyrimidine dendrimers was accomplished by a procedure involving the nucleophilic aromatic substitution (NAS) as a key reaction step by Chavan et al. (2005). The resulting dendritic porphyrin catalysts showed high activity in the light-induced generation of singlet oxygen ($^1\text{O}_2$) from ground-state oxygen. These materials were synthetically useful photosensitizers for oxidation of various olefinic compounds to the corresponding allylic hydroperoxides. Catalytic activities and regio- and stereoselectivities of the dendritic photosensitizers were comparable to those observed for mononuclear porphyrin catalysts. Recycling of the dendrimer-enlarged homogeneous photocatalysts was possible by using a solvent-resistant nanofiltration (SRNF) membrane (oxidatively stable) consisting of a polysiloxane polymer and ultrastable Y zeolite as inorganic filler. Moreover, this membrane technology provided a safe way to isolate the hydroperoxide products under very mild conditions. The membrane showed high retention for the macromolecular catalysts, even in chlorinated solvents, but some oxidative degradation of the porphyrin units of the dendrimer was observed over multiple catalytic runs.

New heterogeneous photocatalytic membranes for oxidation of organic substrates under oxygen atmosphere at 25 °C were prepared by Bonchio et al. (2006) by incorporating decatungstate in polymeric membranes. Polymeric films with a high thermal, chemical, and mechanical stability (PVDF, PDMS, Hyflon) were obtained. The photocatalyst integrity within the polymeric

support was assessed by using various surface techniques including transmittance and reflectance UV-Vis and FT-IR spectroscopies. Catalyst screening was performed under both homogeneous and heterogeneous photo-oxygenation conditions. The photocatalyst activity was evaluated in terms of substrate conversion, turnover numbers, and recycling experiments. A membrane-induced selectivity behavior was evidenced by comparing heterogeneous and homogeneous oxidations.

Photo-oxygenation process using cholesterol (Ch), an important target for oxidative degradation in cell membranes, is described by Andreu et al. (2008) by taking into account two mechanisms: type I (via free radicals) and type II (mediated by $^1\text{O}_2$). Several dyads have been synthesized from beta- and alpha-Ch and ketoprofen (KP) or tiaprofenic acid (TPA). Upon irradiation under anaerobic conditions, KP-alpha-Ch dyads were efficiently photolyzed, via intramolecular hydrogen abstraction from C-7, whereas KP-beta-Ch, TPA-alpha-Ch, and TPA-beta-Ch remained unchanged after prolonged irradiation. The transient absorption spectra of KP-alpha-Ch were assigned to the short-lived biradicals resulting from intramolecular hydrogen abstraction. Interestingly, the spectra and lifetimes obtained for the TPA-derived dyads were very similar to those of the TPA triplet excited state. For the KP-alpha-Ch dyads, generation of $^1\text{O}_2$ was expectedly negligible. Thus, KP-based dyads are appropriate models for type I Ch oxidation mechanism, whereas the TPA derivatives are suitable systems for investigation of the type II mechanism.

The design of new heterogeneous photo-oxygenation systems able to employ visible light, oxygen, mild temperatures, and solvent with a low environmental impact has been investigated by Drioli et al. (2008). In particular, the heterogenization of decatungstate ($\text{W}_{10}\text{O}_{32}^{4-}$), a polyoxometalate with photocatalytic activity in oxidation reactions, was carried out in polymeric membranes of polyvinylidene fluoride. The polymeric catalytic membranes prepared by phase inversion technique were successfully applied in the aerobic mineralization of phenol (used as a probe pollutant molecule) in water. In order to evaluate the effect of the polymeric environment on the overall catalyst behavior, the decatungstate (opportunistically functionalized) was

heterogenized in perfluorinated membrane made of Hyflon. The photocatalytic composite membranes were characterized by different and tunable properties depending on the nature of the polymeric micro-environment, in which the catalyst was confined. Moreover, the selective separation function of the membrane resulted in enhanced performance in comparison with homogeneous reactions.

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Photopolymerization

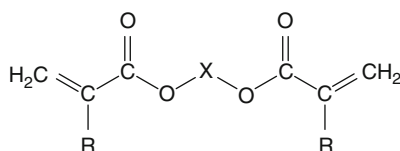
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Photopolymerization has been widely used to produce photoactive polymer-based systems in the coating industry, paints or printing inks, adhesives,

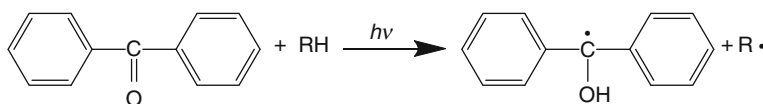
composite materials, and dental restorative formulations (Roffey 1982; Decker and Moussa 1987; Fouassier 1995; Decker 1996; Andrzejewska 2001). The photopolymerization can occur without solvent and within a fraction of a second when intense illumination is used. More importantly, it occurs only in illuminated areas, thus allowing the generation of high-resolution images for the production of complex patterns such as printing plates, optical discs, and microcircuits (Decker 1996; Andrzejewska 2001; Costner et al. 2009).

Acrylate-based monomers have very high reactivity, and therefore, they are the most widely used for photopolymerization. A typical acrylate monomer is shown below:



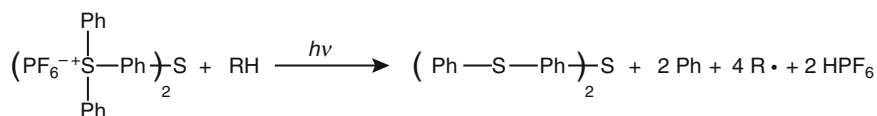
where R = H or CH₃ and X = short-chain alkylene, arylene, polyester, polyurethane, polysiloxane (Andrzejewska 2001).

There are two classes of UV photopolymerization, radical polymerization and cationic polymerization. In the radical polymerization, the free radicals (such as benzoyl radicals) are often produced by homolytic cleavage of C–C bonds or by hydrogen abstraction from an H-donor molecule, as shown below (Decker 1996).



In the cationic polymerization, the protonic acids are often generated by photolysis of onium salts in the presence of an H-donor molecule. The

photolysis reaction can be written as below for a sulfonium salt (Degacure K185), producing both Bronsted acids and free radicals (Decker 1996):

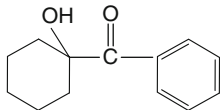


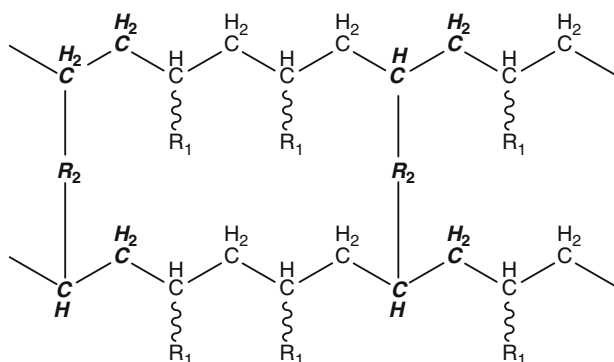
where Ph is the phenyl group.

UV photopolymerization is one of the most efficient methods to generate highly cross-linked polymers from multifunctional monomers

(Andrzejewska 2001). Table 1 shows an example UV photopolymerization using acrylate monomers, PEGDA, and PEAMEA (Lin and Freeman 2005; Lin et al. 2006a, b). The benzoyl radicals are

Photopolymerization, Table 1 Structures of example acrylate monomers and initiator

Chemical	Structure
Poly(ethylene glycol) diacrylate (PEGDA)	$\text{H}_2\text{C}=\text{CH}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\left(\text{O}-\text{CH}_2-\text{CH}_2\right)_{14}-\text{O}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{CH}=\text{CH}_2$
Poly(ethylene glycol) methyl ether acrylate (PEGMEA)	$\text{H}_2\text{C}=\text{CH}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\left(\text{O}-\text{CH}_2-\text{CH}_2\right)_8-\text{O}-\text{CH}_3$
1-Hydroxycyclohexyl phenyl ketone (initiator)	



Photopolymerization, Fig. 1 Schematic representation of PEGDA/PEGMEA copolymer network (Kalakkunnath et al. 2005, 2006; Lin et al. 2006) Italicized and bolded

parts of the network derive from the cross-linker. R1 is CO (OCH₂CH₂)₈OCH₃ from PEGMEA; R2 is COO (CH₂CH₂O)₁₄OC from PEGDA

generated using UV irradiation of 1-Hydroxycyclohexyl phenyl ketone. The structure of the prepared polymer network is shown in Fig. 1.

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Photoreactor

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A photoreactor is a chemical reactor device which brings photons, a photocatalyst, and reactants into

contact, as well as collects the reaction products deriving from physicochemical transformations. It can assume different shapes and modes of operation and can be operated in various environments of temperature and pressure. Design a photoreactor means to establish type, mode of operation, size, and optimal operative conditions. Two general types of photoreactors exist such as batch and plug flow: in the first one, the mixing of reacting mixture is favored as high as possible in order to assume a perfectly mixed reactor, while in the second type, mixing is hindered in order to assume a perfectly segregated reactor. With respect to the operation mode, photoreactors are classified in three general types: (i) discontinuous reactor which during the operation does not exchange matter with the ambient; (ii) semicontinuous reactor which exchanges reagents or products with the ambient; and (iii) continuous reactor, for which there is a continuous and equal inlet and outlet of mass.

The discontinuous reactor is simple and needs only few accessories; it is suitable for experimental kinetics studies, and it is industrially used when the amount of matter to be treated is quite small. The semicontinuous reactor is flexible but more difficult to model; it allows a good control on the reaction rate, as the reaction may be affected by the addition of reagents or by the subtraction of products. The continuous reactor is suitable for industrial purposes when big amount of matter must be treated and/or the reaction rate is extremely high. It needs many accessory devices, but it is possible to achieve a very good control on the product quality (Loddo et al. 2009). The utilization of radiation and solid catalysts in a synergic effect for performing chemical transformations of species present in liquid or gaseous mixtures makes the heterogeneous photocatalytic reactors more complex than the heterogeneous catalytic ones.

The main components of a photocatalytic system are the photoreactor and the radiation. For thermal catalytic processes, the reactor configuration is chosen on the basis of (i) mode of

operation, (ii) phases present in the reactor, (iii) flow characteristics, (iv) needs of heat exchange, and (v) composition and operative conditions of the reacting mixture source (Braun et al. 1991). In addition to previous parameters, the choice of the heterogeneous photoreactors is conditioned by the fact that their geometry and materials must guarantee the penetration of radiation all over the reacting mixture having in mind that the absorbed photon energy should be equal or higher than the bandgap of the used photocatalyst. In the case of stirred photoreactors, the presence of the photocatalyst, usually a powdered micro- or nanocrystalline semiconductor, affects in a complex way the depth of radiation penetration.

Photoreactors and, thus, photocatalytic processes are applicable in wastewater treatment, energy production, chemical synthesis, and greenhouse gas mitigation. They have the potential to address both the consumption of nonrenewable fossil fuels and global warming, two of the greatest problems facing humankind. The state-of-the-art in solar photoreactor design to assess those systems which are most applicable for industrial-scale implementation has been reviewed by Braham and Harris (2009). Designs for parabolic trough, compound parabolic, inclined plate, double-skin sheet, rotating disk, water bell, fiber optic, and fixed/fluidized bed photoreactors are qualitatively discussed and compared. Compound parabolic photoreactors are most suited to near-term applications at pilot scale (>1000 L/day) due to their advantageous light-collecting properties and well-known design methodology.

Engineered photocatalysts, photoreactor systems, process optimizations and modelings of the photooxidation processes for water treatment, and a number of potential and commercial photocatalytic reactor configurations, in particular the photocatalytic membrane reactors, are discussed by Chong et al. (2010). The main technical barrier that impedes commercialization of semiconductor photocatalytic process was the post-recovery of the catalyst particles after water treatment. But, nowadays, membrane photoreactors have shown to solve this drawback (Molinari et al. 2002).

The existence of mass transfer limitations in slurry photocatalytic reactors and experimental validation was made in a flat reactor that was part of a recycling system by Ballari et al. (2010). When the photocatalytic reaction is not fast, employing catalyst loadings below 1 g L^{-1} , irradiation rates at the reactor wall below $1 \times 10^{-6} \text{ Einstein cm}^{-2} \text{ s}^{-1}$, and good mixing operation ($\text{Re} > 1700$), mass transport limitations in the bulk of the fluid can be considered virtually nonexistent.

The photocatalyst with designed physicochemical properties is the key in the process. Recent research progress toward the design and preparation of porous photocatalysts with structural, compositional, and morphological properties suitable for use in a photocatalytic reactor for water treatment via advanced oxidation processes have been reviewed by Pan et al. (2010). Various synthetic strategies for fabricating porous photocatalysts with well-defined microscopic morphologies and nano/mesoscopic active nanobuilding blocks and the synthesis-component-structure-property relationship working in photocatalyst design are discussed.

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Physical Cleaning

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Physical cleaning methods generally involve applying hydraulic or mechanical forces to dislodge and remove foulants from the membrane surface. In the course of filtration, diverse phenomena might occur, causing the reduction of the membrane performance. The deposition of solutes and/or particles onto the membrane surface (cake layer formation) or into membrane pores (pore blocking) is one of the main challenges in the operation of membranes, causing flux decrease and/or the increase of the transmembrane pressure (TMP). Whereas physical cleaning can remove reversible fouling, the irreversible one can be only reduced by chemical cleaning. Conventional physical cleaning techniques are based either on hydraulic (forward and reverse flushing, backwashing, membrane relaxation, and air flushing) or mechanical (sponge ball and fluidized particle cleaning) methods. Regarding the cleaning by sponge balls and fluidized particles please refer to mechanical cleaning. Ultrasonic and electrical fields are innovative and emerging cleaning methods that were developed in recent years to overcome the limitations of the commonly used methods and are discussed as nonconventional cleaning strategies. The optimum physical cleaning is closely linked to the nature of fouling.

Conventional Cleaning Methods

Forward and reverse flushing removes foulants by pumping permeate water at high crossflow velocity across the membrane surface facing the retentate side. Because of the more rapid flow and the resulting turbulence, particles absorbed to the membrane are released and discharged. In the reverse flushing method the direction of the permeate flush is alternated for a few seconds in the

forward (feed to brine) and in the reverse direction (brine to feed). Forward flush techniques are particularly useful in removing colloidal matter (Arnal et al. 2011).

Backwashing is a reversed filtration process, in which permeate is flushed through the membrane to the feed side to achieve high shear at the membrane surface. In porous membranes, backward flush results in flushing the pores inside out (Arnal et al. 2011). Periodic backwashing of membranes, usually for a few minutes, at a flux being at least two times higher than the typical filtration flux, is very effective in removing fouling and thus decreasing pressure to the previous low value. Since physical cleaning only removes reversible fouling (Baker 2004), the average pressure still shows a gradual increase with time and chemical cleaning will be necessary to overcome irreversible fouling (Baker 2004). Backwashing is fully automatic, initiated at a fixed interval of operation or once TMP reached a set point (Villarreal et al. 2013). A backwash can only be applied for ceramic, hollow fiber, tube, and some flat sheet ultra- and microfiltration (MF) membranes as backwashing of spiral wound membranes would damage the glue layers of the membrane elements. Backwashing effectiveness depends on the nature of the fouling mechanism it deals with. The more adherent the foulants are, the higher forces are required to minimize fouling (Shi et al. 2014). Although backwashing results in beaks in operation, an increase of energy consumption, and the loss of permeate, it has been widely applied in industry.

Membrane relaxation refers to the periodical break of the filtration process and thus allows concentrated foulants at the membrane surface to diffuse away by diffusive back transport in “relaxed” conditions. Membrane relaxation is suitable for removing reversible fouling only, allowing filtration to be maintained for longer periods before the need for further cleaning. A further enhancement of the process may be ensured by combining relaxation with air scouring, which creates the shear along the membrane removing foulants more effectively (Hong et al. 2002). As opposed to backflushing, this method does not involve the permeate loss; however, it

reduces overall flux, and therefore higher membrane surfaces are needed.

Air flushing (air sparging, air scouring). By using mixture of water and air during membrane cleaning, increased turbulence is achieved that results in high shear forces at the membrane surface improving the removal effectiveness of fouling. Air sparging can be applied either during the course of filtration to reduce fouling deposition or periodically to remove already formed deposits (Cui and Taha 2003; Shi et al. 2014). In ultrafiltration (UF) systems, air is usually introduced periodically into the flushing stream before backwashing takes place. In order to keep filtration process with good productivity, air flushing can be used as a continuous fouling control method, pumping air continuously into the feed stream. Hence, a two-phase flow (gas/liquid) formed parallel to the membrane surface can reduce concentration polarization and control external fouling to some extent (Laborie et al. 1997; Cui and Taha 2003). There are several flow patterns possible depending on the superficial liquid and air velocities; however, slug flow is the most effective pattern to enhance mass flow (Psoch and Schiewer 2006). Air sparging is typically applied in MF and UF membranes, and it seems to work best for tubular and flat sheet membranes and to a lesser extent in hollow fiber and spiral wound modules (Cui and Taha 2003). Parameters such as the type of membrane module, the duration of air flushing, the air velocity, and the size of the air bubbles just to name a few have effects on the cleaning efficiency. The negative side is that compressed air has the potential to cause damage to membranes.

Nonconventional Cleaning Methods

Another method for generating mechanical action is the use of *ultrasound waves* that result in the cavitation of fluids and the consequent increase of turbulence and shear forces on the membrane surface. Frequencies of ultrasound can range between 16 and 1,019 kHz and are generated by electromechanical transducers based on piezoelectric effect. At these high frequencies

cavitation bubbles are promoted by the pass of the ultrasonic waves through the liquid medium in a series of alternate compression and expansion phases promoting their formation, growth, and implosive collapse in the liquid (Arnal et al. 2011). Ultrasound irradiation, caused by the liquid jet, enhances the membrane flux by decreasing the thickness of boundary layer (concentration polarization) and diffusional resistance at the membrane surface (Arnal et al. 2011). According to Wu et al. (2013), while applying an ultrasonic field, also chemical effects happen, i.e., radical species may be formed during cavitation. There are a number of parameters that influence the effectiveness of ultrasound cleaning, i.e., frequency, power intensity, feed properties, membrane properties, crossflow velocity, temperature, and pressure. Some evidence of damage to membranes due to ultrasound irradiation may occur. First, erosion caused by the radicals formed from sonolysis on the membrane surface can be a major concern. Secondly, the ultrasonic cleaning cannot be applied to all membrane materials. Therefore, membrane durability during ultrasound treatment should be taken into account. Despite the considerable potential of ultrasound-induced membrane filtration, the cleaning method has not yet been widely commercialized. The main reasons that this method has been limited up to now are the development stagnation of transducer technology for membrane filtration and the control of membrane erosion (Arnal et al. 2011; Shi et al. 2014).

Pulsed *electric fields* are also used to clean membranes by applying the pulsed fields of a short duration throughout the filtration process on a periodic basis. An electric field is generated by placing two electrodes on either side of a membrane. In some cases only one electrode is used when a membrane itself is made of conductive material, hence acting as an electrode. This cleaning method is very effective at reducing the concentration polarization layer and removing particulate foulants, as the applied electric field can induce charged particles to move away from the membrane surface toward the electrode with the opposite sign. The main mechanism on which the electrical cleaning is based refers to electrophoresis. Besides the occurrence

of electrophoresis, other effects such as electrolysis, Joule heating, or ion migration also happen, which can affect filtration performance and fouling process. The process can be applied for flat sheet and tubular membranes with platinum electrodes. Operation can be applied to crossflow as well as to dead-end configurations (Ahmad and Ibrahim 2002). Electric fields have been also recently applied to membrane bioreactors (MBRs), so-called EMBRs (electric field-attached MBRs). The electric field strength (E) is an important parameter in the operation of electric fields and depends on frequency, feed conductivity, properties of the solutes (concentration, zeta potential, and charge), electrode placement, and material having effect on electric cleaning (Arnal et al. 2011; Shi et al. 2014). Process used to be enhanced by the presence of dynamic turbulence promoters as static metal deployed sheet, oxygen bubbles, or activated alumina in UF membranes (Mameri et al. 1999). As opposed to the conventional physical cleaning strategies, this method involves no significant loss of permeate during the pulse and can be running without interruption. The limitation of this cleaning method is the high energy demand for application of an electric field. The energy consumption could be however kept lower due to the application of the intermittent (pulsed) operation. Moreover, electric fields may also affect biological activities, i.e., through stimulating the secretion of extracellular polymeric substances from cells which contribute to membrane fouling (Von Zumbusch et al. 1998).

Cross-References

- Fouling
- Mechanical Cleaning
- Permeate
- Retentate
- Ultrafiltration (UF)

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Physical Pretreatment

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Definitions

The term *physical pretreatment* refers to the use of a physical barrier of filtration media to remove particulate contaminants from a liquid phase. In

a pretreatment duty, the media is porous, having a regular structure which can retain particulates while allowing the carrier fluid to flow through the media.

Objectives

The objective of physical pretreatment is to remove particulates which would otherwise foul downstream processes. The specification of the pretreatment media is selected to ensure stable operation for the next treatment stage, which could be, for example, disinfection, reverse osmosis, ion exchange, or an advanced oxidation process.

Description

Physical pretreatment equipment normally falls into one of the following categories:

- Membrane filtration
- Cartridges
- Screens

The characteristic of each of these types of process is that the aperture or media porosity which defines the physical barrier can be precisely controlled to achieve the required level of contaminant removal. For membrane filtration, the aperture would be the size of the pores in the porous media used to create the membrane surface in contact with the feed (Mulder, 1996). For cartridges, the media openings can be created between the strands of material used to make up the media or in the surface porosity of the material chosen. For a screen, the aperture could be determined by the mesh size of the media used or the assembly tolerance of media layers in forming the device.

Granular media filters such as sand filters could also be used to provide a physical filtration barrier. However, granular media filters do not normally achieve a sufficient removal on their own and are therefore often used as part of a more comprehensive treatment train incorporating the use of

chemical preconditioning (see “► [Granular Media Pretreatment Filtration](#)”). Membranes are also sometimes used after a chemical pretreatment stage, but they are just as likely to be used as a simple physical barrier.

Particle Removal Mechanisms

Particle removal in physical pretreatment can be by one of the two mechanisms, i.e., surface removal or depth removal. In a surface removal device, particles are prevented from entering the media due to the fine pore or aperture size at the surface. Particles therefore accumulate at the surface until transported away by bulk fluid flow, or by backwash or cleaning, or by disposal or removal of the media. The capacity of a surface removal mechanism device is relatively low, so the disposal option is unusual. However, it is sometimes used for valuable feedstreams or where there is a very low particle challenge, for example, ensuring that an ultrapure water loop remains particle-free.

A successful surface removal device needs to have an extensive surface and/or an effective cleaning or particle removal mechanism. The part of the media below the surface provides mechanical support and is normally relatively thin and porous so that it does not create an unnecessary resistance to flow. It is important for this type of device that the media surface has a consistent pore or aperture size (i.e., a narrow pore size distribution or consistent mesh structure). Below the surface, any supporting structure needs to confer sufficient strength to ensure robustness and long-term integrity of the separating layer. Membranes and screens use the surface removal mechanism.

The other separation mechanism used in physical pretreatment devices is depth removal. A depth removal device operates by allowing a proportion of the particle challenge from the feed to pass through the media. Particles are then captured within the media structure rather than being retained at its surface. The advantage of this mechanism is that the particle loading of the media is much greater than for a surface filtration

Pore Size, μm	0.001		0.01		0.1		1		10		100	
Approx equiv MWCO, kDa	2-5		100		500-1000							
Relative Size of Common Material	Salts Metal ions DOC		Pyrogens Sugars		Virus Colloidal silica		Bacteria		Yeast cells		Sand	
Membrane Technology	RO		Process UF	UF	MBR		Nominal Cartridge		Screens			
		NF			MF		Sterilizing Cartridge		Granular media filters			

Physical Pretreatment, Fig. 1 The filtration spectrum for physical pretreatment

device. The disadvantage is that the device cannot be relied on to remove all of the target particles since having entered the bulk of the media, they may evade all potential capture sites. Also, it may be difficult to remove the particles once captured. It is quite common therefore to dispose of the media when fully loaded rather than try to clean or regenerate it. Cartridges often use the depth removal mechanism.

Membrane Filtration Products

The separation spectrum for filtration devices is illustrated in Fig. 1. The term membrane filtration is used to describe the processes of ultrafiltration (UF) and microfiltration (MF) (Zeman & Zydney, 1996). UF membrane normally used for pretreatment have a pore size of around 0.01–0.02 μm , though finer UF is also used for process duties. The MF pore size for pretreatment normally ranges from 0.04 to 0.1 μm , though there are coarser MF membranes for other duties. Below the size range of UF is the membrane process nanofiltration (NF) with a pore size of around 0.001 μm or 1 nm. This can be used for pretreatment, but is more likely to be the recipient of a UF or MF pretreated feedstream. However, the most common process following membrane pretreatment is reverse osmosis (RO), since this technology is particularly sensitive to particulate fouling due to the characteristics of the spiral wound element format often used.

UF membranes often use a hollow fiber format with a polymeric membrane material having an

asymmetric structure. A fine porous surface or active separation layer is supported by a more porous open structure, as shown in Fig. 2. In MF, the pore structure through the wall is symmetric or with limited asymmetry. This ensures that the fiber has sufficient strength when differential pressure is applied to drive flow through the structure. Ceramic materials are also used for UF and MF in process duties, and recently there has been an uptake of ceramics for water applications.

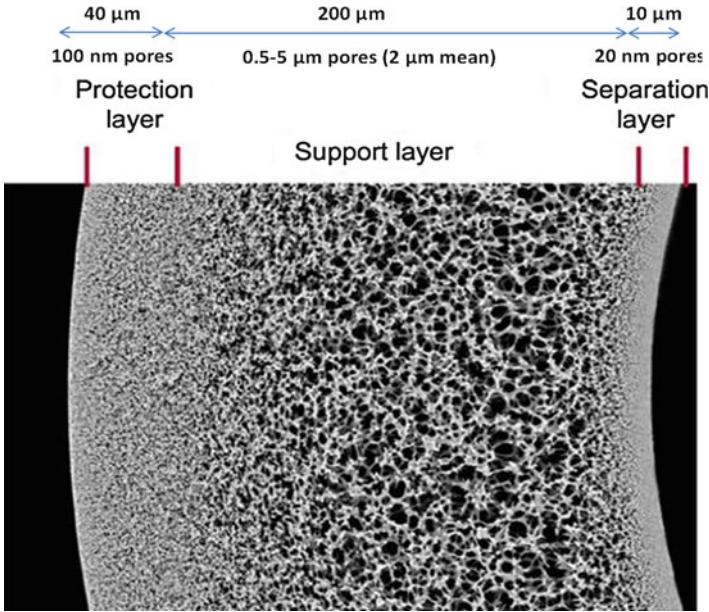
Cartridge Products

Membrane cartridges are made from a porous membrane, potentially cast onto a support medium. Depth cartridges are made by winding a polymer thread or string around a former to create a porous depth network. A supported membrane media for use in a membrane cartridge is shown in Fig. 3.

This type of cartridge provides an absolute filtration barrier like a membrane filtration process. Since membrane cartridges are normally difficult to clean, they are used for feeds with a low solid loading.

The thread or string wound depth cartridge provides a nominal removal rating and is utilized for noncritical duties. A nominally rated cartridge is often used for very good consistent feeds to provide a minimal filtration duty prior to RO or other advanced treatment. This type of cartridge is also used after other pretreatment processes to provide an inexpensive guard duty in case of breakthrough, equipment failure, or unexpected

Physical Pretreatment,
Fig. 2 Typical PES hollow
fiber UF membrane cross
section (Courtesy of
Membrana, Germany)



Physical Pretreatment,
Fig. 3 Typical membrane
structure used in a
membrane cartridge



contamination. Since most cartridges are not cleanable, they tend to be only used for duties in which the solid loading is expected to be low.

Backwashable cartridges can be used, and there are various proprietary devices in use. However, it is not common to find them used for pretreatment applications.

Screen Products

In the context of physical pretreatment, screens are used as a preliminary pretreatment stage, often providing protection to other pretreatment devices. It is common to use screens as a pretreatment to membrane filtration, since membrane products have a limit as to the size of

particle that can be accepted in the feed. The nominal rating for a screen in this type of duty is typically between 50 and 300 μm. Screens are not normally used for other filtration devices such as granular media filters, since this same limit to the influent feed quality does not apply.

The simplest screens are formed from wire mesh. The media is cleanable and can use either an automatic backwash mechanism or could be cleaned manually in situ, or the media could be removable for manual backwash. Since the mechanism is that of surface filtration, the dirt holding capacity is not that great; hence, cleaning is relatively frequent if there is a significant feed challenge.

Coarse screens may use a different media, and an example is the bar screen used for membrane

bioreactor pretreatment, which requires a rating of 0.3 mm or higher.

At the finer end of the spectrum, it is possible to get screens with a fine rating of 20 μm or even less. However, it would be unlikely that this rating would be fine enough for direct pretreatment to RO and would be unnecessarily fine for a preliminary stage prior to membrane pretreatment.

Fouling Mechanisms

Particle removal technologies are prone to fouling by the challenge that they are trying to remove (Pearce, 2011). A simplified representation of the two main physical fouling mechanisms is shown in Fig. 4. If the pore or aperture openings of the media are larger than the particles that are being removed from the feed, they may enter the throat of the pore and block the pore from contributing to flow. The second mechanism shows a high concentration of particles of different sizes congregating near the pore openings and causing a cake layer to build up. As the cake layer develops, it effectively becomes the filtration medium since it prevents particles approaching the surface.

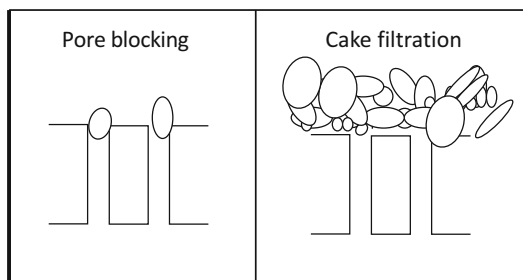
For physical pretreatment devices that rely on a surface filtration mechanism, the openings of the media (i.e., the mean pore size and the pore size distribution) have to be carefully selected to avoid the pore blocking phenomenon, also known as pore plugging. Thus, for water treatment applications in which there is a low solid loading but a high concentration of fine particles, an ultrafiltration (UF) membrane might give a more stable

performance than microfiltration (MF). In wastewater, which has a higher concentration of larger particles and the presence of floc particles, MF is often selected. The process design required to prevent the accumulation of solids at or near the surface is discussed in the next section.

The consequence of fouling is that the differential pressure rises if flow is maintained, either due to the restriction in the number of pores available or due to the additional resistance for the feed to transfer across the developing cake layer or a combination of both. As fouling progresses, there comes a point at which differential pressure rises sharply, which indicates that the useful productive cycle is at an end. Increasing pressure under these conditions can force particles further into the pores and/or cause the cake layer to compress becoming less permeable, and both of these effects can be difficult to reverse in the cleaning cycle.

For a device which operates by a depth filtration mechanism, the media is selected to ensure that particles can penetrate the surface, so that they can subsequently be captured in the depth of the bed, thereby ensuring a high dirt holding capacity. If the particle concentration is excessive for the media pore size selected, a cake will form on the surface, significantly reducing the life of the filter. This phenomenon is referred to as surface blinding, since there is normally no mechanism employed to control the effect or reverse it if it happens.

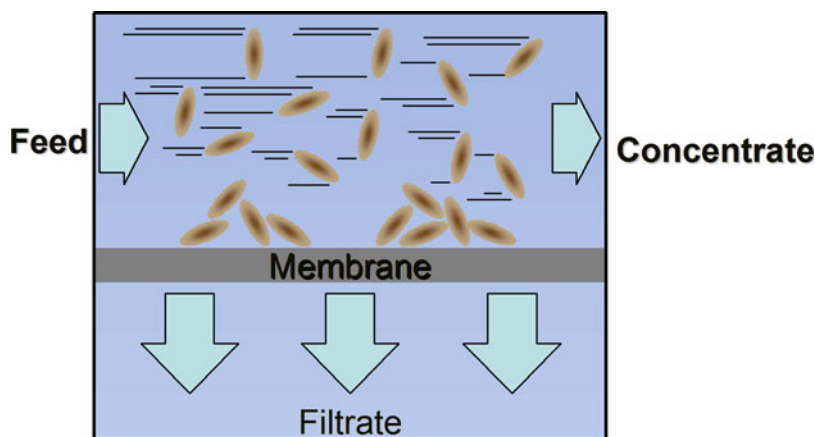
Process Design for Surface Removal Devices



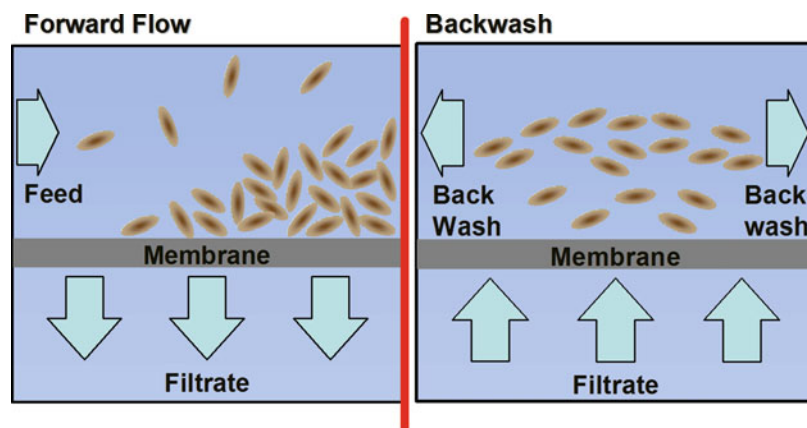
Physical Pretreatment, Fig. 4 Particle fouling mechanisms

Membranes and screens are the two most common types of device that use a surface removal mechanism. There are two possible process designs for their operation, and they will be illustrated in this section by reference to normal process design terminology and operating parameters encountered in membranes. For membrane systems, the two process design options are referred to as either crossflow or dead end with backwash, sometimes known as directflow. In crossflow, the carrier fluid sweeps across the surface of the media, preventing

Physical Pretreatment,
Fig. 5 Crossflow process
 flow scheme



Physical Pretreatment,
Fig. 6 Directflow process
 flow scheme



an excessive accumulation of particles, as shown in Fig. 5. If possible, it is desirable to use a velocity high enough to create some degree of turbulence, but in practice, the feed channel dimensions for water treatment products are often too narrow for that to be practical without an excessive pressure loss on the feed side. A narrow feed channel gives a high packing density, which reduces capital cost for high flow applications.

The bulk carrier fluid passes through the media to provide a particle-free filtrate on the other side. The disadvantage of crossflow is that even at modest velocities, the energy cost is prohibitive for many applications, particularly in water and wastewater treatment. An alternative approach is to use a directflow process flow scheme as shown

in Fig. 6. Directflow is suitable for feed streams that do not contain an excessive concentration of solids, and this applies to most feeds in the water and wastewater industry. It is possible to use this approach for feeds containing 100 ppm of total suspended solids or more, but most duties for which this approach is used have less than 10 ppm.

Feed is passed into the feed channel during a filtration cycle, which typically lasts for 20–60 min. For a hollow fiber membrane, the feed channel can either be inside the fiber lumen (known as the inside feed format) with filtrate withdrawn through the shell or module housing. Alternatively, the feed can be on the outside or shell side of the fiber (the outside feed format) with filtrate withdrawn from the lumen. For either

format, the process sequence has similarities. Particles are retained within the feed channel, accumulating at the dead end, which is a closed valve, signified in red. As with crossflow, the bulk carrier fluid passes through the membrane to provide a particle-free filtrate.

Periodically, a short backwash or cleaning cycle then takes place which removes the accumulated solids from the surface. The cleaning cycle may be assisted by air for the outside feed format and in some cases is conducted by draining fluid from the feed channel while applying an air scour. At the end of the cleaning cycle, which is normally complete in a minute or less, feed flow is reintroduced to the feed channel and a new filtration cycle begins. The concentrated backwash constitutes a waste stream which might be reprocessed to enhance recovery.

The process design for the operation of screens is normally dead end with backwash. Particles retained by the media in the filtration cycle are then removed by a high pressure reverse flow to ensure that they are flushed out on the media effectively in a short backwash cycle.

Process Design for Depth Devices

A depth filtration device such as a cartridge operates like a dead end or directflow process, but without backwash. The dirt holding capacity is sufficient to allow the cartridge to operate for a reasonable length of time until the capacity is exhausted. The cartridge is then removed and replaced. It is possible with some cartridges to remove and clean the media, but normally they are disposed of. If the cartridge is performing a guard duty, the economics of disposal are acceptable since the loading is low, but feed upsets can cause excessive replacement.

It is important to choose the correct rating and type of cartridge since the particles should not bridge the pores at the surface, but penetrate the depth, or the extensive dirt holding capacity provided by the depth of media will not be utilized and cartridge life will be short. However, if the pore size selected is too open, fine particles will contaminate the filtrate, which

might mean that the pretreatment duty is not performed effectively.

Cross-References

► [Polymer with Intrinsic Microporosity \(PIM\)](#)

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Physically Irreversible Fouling

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Antonyms

► [Physically reversible fouling](#)

Physical cleaning of the membrane (e.g., by rinsing, relaxation, backwashing) is generally not able to remove all the fouling materials present on the membrane surface. The fraction of fouling remaining on the membrane surface is defined as physically irreversible fouling. As the level of physically irreversible fouling increases with continuous filtration, the filtration becomes unsustainable, and chemical cleaning is generally conducted in order to remove a greater portion of fouling materials.

Given that physical cleaning is expected to remove more of the large fouling materials having low level of interactions with the membranes, physically irreversible fouling will be due to

smaller compounds able to enter the pores of the membranes or having strong interactions with the membrane polymers. They will include small organic compounds (biopolymeric substances, such as proteins, carbohydrates, humics, and smaller building blocks) and inorganic scales.

Cross-References

► [Reversible Fouling](#)

Physically Reversible Fouling

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Antonyms

► [Physically irreversible fouling](#)

In order to remove a portion of the fouling formed during membrane filtration, physical cleaning is generally conducted. Strategies including relaxation (during which, filtration is paused for few seconds up to a minute) and backwashing (during which, permeate is pumped in the reverse direction back into the membrane) are commonly applied for low-pressure systems such as microfiltration (MF) and ultrafiltration (UF). Recently, relaxation and osmotic backwash have also been considered for nanofiltration (NF) and reverse osmosis (RO) (Ramon et al. 2013)

In MF and UF, materials responsible for physically reversible fouling are generally large particulate/colloidal compounds, having low degree of interactions with the membrane surface and because of their large size, being easily removable by relaxation and backwashing. During relaxation (and the absence of flux-induced dragging forces), the deposited materials on the surface of the

membrane tend to detach due to the shear rate still applied in the feed bulk. In the case of backwashing, some of the smaller compounds (biopolymers, colloids) entrapped within the pores of the membranes can also be dislodged and pushed back into the feed stream.

Physical cleaning is generally implemented in addition to other continuous fouling control strategies (i.e., operating conditions used to limit the extent of fouling during filtration, including high feed cross flow velocities, aeration, etc.).

Although physical cleanings are used on a frequent basis, their efficiency is known to decrease with filtration time. As irreversible fouling accumulates on the surface, chemical cleanings of various intensities (i.e. higher concentration of the cleaning agent) can be applied on a weekly to yearly basis.

Cross-References

► [Reversible Fouling](#)
 ► [Reversible Fouling Resistance](#)

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Pineapple Juice, Ultrafiltration of

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Pineapple is one of the most appreciated tropical fruits due to its very attractive aroma, flavor, and other beneficial components.

Numerous in vitro studies have reported its high antiradical activity and capacity to inhibit the human low-density lipoprotein and liposome oxidation. Biochemical and pharmacological

activities have been attributed to free radical scavenging, effect on immune and inflammatory cell functions, and antitumor properties.

The conventional pineapple juice processing is often accomplished by some drawbacks such as browning, formation of haze/precipitates, and flavor changes which limit the production of high-quality juices. For example, conventional clarification of pineapple juice involves many steps, such as enzymatic treatment (depectinization), cooling, flocculation (gelatine, bentonite, and diatomaceous earth), decantation, and filtration, requiring more costs with personnel, equipment, and physical space.

Ultrafiltration, a pressure-driving membrane process, is considered one of the alternative methods for pineapple juice production.

UF process permits to retain large species such as microorganisms, lipids, proteins, and colloids, while small solutes such as vitamins, salts, and sugars flow with water. The advantages of UF process over conventional pineapple juice clarification are increase of juice yield; possibility to operate in a single step and to reduce working time; reduction in enzyme utilization; easy cleaning and maintenance of equipment; possibility of avoiding the use of gelatines, adsorbents, and other filtration aids; elimination of need for pasteurization; and reduction of waste products. In addition, the UF process, working at room temperature, preserves the natural pineapple fruit constituents, the juice freshness, as well as the volatile aroma profile avoiding the deleterious effect of thermal treatment, such as sugar caramelizing and browning. This process is typically used to separate the pineapple juice into a fibrous concentrated pulp (retentate) and a clarified fraction free of spoilage microorganisms (permeate).

Permeate fluxes and quality of clarified pineapple juice are strongly affected by operating conditions, such as cross-flow velocity, transmembrane pressure, temperature, volume reduction factor (VRF), and membrane properties such as membrane material (polymeric or ceramic) and molecular weight cut-off (MWCO).

Polysulfone and ceramic membranes with a MWCO in the range of 30–100 kDa have been extensively used for pineapple juice UF (de Carvalho et al. 1998; Laorko et al. 2010).

A 100 kDa PS membrane permitted a good level of clarification of pineapple juice reducing totally the suspended solids and the turbidity of the juices. The clarified pineapple juice presented physicochemical and nutritional properties comparable with those of fresh fruits in terms of vitamin C, total phenolic content, and antioxidant activities.

A major limiting factor in pineapple juice UF processes is the declining permeate flux (J) with time (t) reducing process efficiency. This decrease is caused by the accumulation of macromolecular or colloidal species (such as pectin material, tannins, protein, and fiber) on the membrane surface (concentration polarization and gel layer) or the possible precipitation of smaller solutes in the membrane pores (fouling).

The complete pore blocking and cake formation are the main mechanisms involved in the UF of pineapple juice with ceramic tubular membranes and polysulfone hollow fiber membranes, respectively (de Barros et al. 2003).

The clarified pineapple juice can be used in the manufacture of different products such as liqueurs, cocktails, fizzy beverages, and flavored mineral water. Moreover, the bioactive compounds present in the permeate fraction may be used in the pharmaceutical and food industries for the production of nutraceutical and as food formulations. The clarified pineapple juice can be submitted to a concentration step by using thermal evaporation or membrane operations such as reverse osmosis (RO), osmotic distillation (OD), and membrane distillation (MD).

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Plasma Etching

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Plasma etching (Yasuda 1985; d'Agostino 1990; Biederman and Osada 1992; Inagaki 1996) is one of the major effects caused by the interaction between a cold plasma (defined in the article entitled "Vapor plasma membrane treatment") and a material placed within it. It is due to combination of reactive species of the gas phase with atoms or groups of atoms of the substrate leading to the creation of active sites on the surface of the substrate (ablation of surface) and to the formation of volatile species which diffuse in the gas phase. Plasma etching is prevalent on the other plasma treatments (plasma functionalization, PECVD/plasma polymerization) in the case of inert gases such as rare gases (argon (Ar), helium (He)), O₂, SF₆, or C_xF_y used as gaseous phases.

Plasma etching is mainly used for the surface modification of polymers or metals. In the case of a polymeric substrate, plasma etching is systematically coupled with substrate cross-linking due to opening (under the action of the reactive species of plasma) of the bonds between atoms of the surface of the substrate allowing them to reorganize (by bridging between the macromolecular chains). The main application of plasma etching is certainly the preparation of MEMs in microelectronics. In the field of membranes, the implementation of plasma etching has appeared in the last decade. Plasma etching has been applied for modulating the membrane transport properties (by cross-linking the surface chains, increasing the pore size, or etching the polluted surface) or reinforcing their mechanical, thermal, and chemical stability (essentially under the effect of cross-linking) (Bryjak et al. 1996; Gancarz et al. 1999; Reinholdt et al. 2012). However, it is generally known that, in the case of some specific polymer membranes, the effect gained in such modifications may disappear or significantly diminish during storage. Moreover, plasma etching can

sometimes alter the physicochemical properties of material and particularly polymer surfaces.

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Plasma Functionalization

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Plasma functionalization (Yasuda 1985; d'Agostino 1990; Biederman and Osada 1992; Inagaki 1996) is one of the major effects caused by the interaction between a cold plasma (defined in the article entitled "Vapor plasma membrane treatment") and a material placed within it. It is due to fixing of reactive species of the gas phase on active sites of the surface of the substrate. Plasma functionalization is prevalent on the other plasma treatments (plasma etching, PECVD/plasma polymerization) in the case of chemically reactive gases such as ammonia (NH₃), nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), water vapor (H₂O), tetrafluoromethane

(CF₄) . . . used as gaseous phases. More precisely, plasma functionalization consists in grafting of amine-type or amide-type functional groups in the case of NH₃ or N₂, grafting of peroxide or hydroxide functions in the case of O₂ or H₂O, grafting of C=O, C-OH, C(=O)OH functions in the case of CO₂, and grafting of CF_x functions in the case of CF₄. In the case of a polymeric substrate, plasma functionalization is systematically coupled with substrate cross-linking due to opening (under the action of the reactive species of plasma) of the bonds between atoms of the surface of the substrate allowing them to reorganize (by bridging between the macromolecular chains).

Plasma functionalization is mainly used for the surface modification of polymers or metals. In the field of membranes, the implementation of plasma functionalization has grown rapidly in the last decade. Plasma functionalization has been especially applied for improving the wettability, printability, adhesion, or biocompatibility of conventional polymer membranes, modulating their transport properties (by changing the hydrophilic/hydrophobic balance, providing the grafting of specific functional groups or cross-linking the surface chains), or reinforcing their mechanical, thermal, and chemical stability (essentially under the effect of cross-linking) (Roualdes et al. 2010).

However, it is generally known that, in the case of some specific polymer membranes, the effect gained in such modifications may disappear or significantly diminish during storage. Moreover, plasma functionalization can sometimes alter the physicochemical properties of material and particularly polymer surfaces. An efficient way to overcome this limitation is the implementation of a process named plasma-induced graft polymerization or plasma grafting. In this process, plasma is used only to create on the polymer surface functionalities that are able to initiate conventional polymerization of monomers containing multiple bonds. The reaction may be carried out in two ways: in the vapor phase of monomer or in solution. Its principle is the following. Plasma treatment can induce radical formation on polymers surface through ion bombardment and UV

radiation. The radicals formed on the surface of the treated polymers can be very stable in vacuum but react rapidly on exposure to a reactive gas. So if the vapor phase of an unsaturated monomer is introduced into a plasma reactor just after the surface treatment of a polymer substrate, the radicals formed on the surface of the polymer substrate immediately cause the polymerization of the monomer. The process can also be implemented in solution. In this case, the polymer substrate is released from the reactor after the plasma treatment and then exposed to atmosphere. In the presence of oxygen or air, peroxides and hydroperoxides are created on the polymer surface; such functions may initiate the polymerization of a desired monomer in solution. In both cases (vapor phase route or solution route), grafting density and length of grafted brush can be regulated to some extent by plasma and grafting parameters. One primary advantage of this technique is the ability to modify surface properties of the polymer substrates permanently without affecting the bulk mechanical and chemical properties. There have been several reports on hydrophilization of polysulfone surface after plasma treatment by plasma-induced graft polymerization (Inagaki et al. 1997; Muller et Oehr 1999; Liu et al. 2005).

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Plasma Membrane

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Plasma membrane names either a conventional membrane which has been modified on the surface by a plasma treatment (plasma etching, plasma functionalization, PECVD/plasma polymerization), called plasma-treated membrane, or a plasma polymer deposited on a highly porous substrate (which plays the role of mechanical support) having specific separation properties, called plasma-polymerized membrane (see article “plasma polymerized membrane” for more details).

The first developed plasma membranes have been intended to gas permeation or retention and also pervaporation. As a striking example relative to plasma-treated membrane for gas permeation, Kumazawa et al. studied the gas perm-selectivity of polyethylene (Nakata and Kumazawa 2006) and polypropylene (Teramae and Kumazawa 2007) membranes after a 5 min long N₂ or NH₃ plasma treatment. They found that nitrogen was not significantly incorporated to the polymer network and that CO₂ permeability coefficients slightly increased after the plasma treatment, whereas N₂ ones were not affected, which places these plasma-treated polymer membranes over classical glassy polymers like polyimides, in terms of CO₂ separation factor. Vilani et al. (2007; Weibel et al. 2007) studied polyurethanes membranes used to separate methanol from methyl-t-butyl ether by pervaporation after an acrylic acid vapor plasma treatment. They

showed that a short-time modification with a high plasma input power (100 W) allowed to increase the selectivity factor from 5 to 30 and also the permeate flux (Vilani et al. 2007). They attributed these evolutions to an increase of C=C contribution and a loss of C–N content that might result in a cross-linking at the surface due to decreases of the surface-free volume and chain flexibility. Upadhyay and Bhat (2004) proved the strong efficiency of a nitrogen plasma treatment compared to oxygen or air plasma treatments of nonporous polyvinyl alcohol-based membranes. The extremely high selectivity of the nitrogen-treated membranes toward water molecules (over 1,200 in isopropyl alcohol (IPA) – water mixture with IPA weight fraction below 0.8) could be attributed to the surface cross-linking, whereas air and oxygen plasma-etched amorphous regions decrease the swelling of the treated membranes and their selectivity to water.

More recently, plasma membranes have been prepared for liquid separation processes. A lot of works have been devoted to polysulfone (PSU) membranes widely used in microfiltration or ultrafiltration processes, in particular for low-protein adsorption in serums and plasma. There have been several reports on hydrophilization of PSU surface after plasma treatment by noncondensable gases, plasma-induced graft polymerization, or plasma polymerization (Roualdes et al. 2010). Selective membranes for the separation of water from hydrophobic liquids can be obtained by depositing a hydrophobic plasma-polymerized thin layer on porous materials such as filter paper or polyester textile (Bankovic et al. 2004). The development of plasma membranes has been more recently applied to fields using ion-conducting membranes such as electromembrane processes (electrodialysis in particular), electrochemical sensors, or, more broadly, the energy production devices (fuel cells, Li-ion batteries, etc.) (Roualdes et al. 2010).

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► Cellular Membranes

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Plasma Polymerization

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Plasma polymerization is the other name of PECVD in the case of vapors of organic compounds as gaseous phases (the most case in the field of membranes). Plasma polymerization has little in common with classical polymerization. Many side reactions occur during film deposition. This can be understood by the poor selectivity of the breaking up of chemical bonds in a plasma. The mechanism of deposition is not yet well understood. This difficulty arises from the complexity and variety of active species, reaction steps, and dependences on plasma parameters. Several kinetic models of plasma polymerization have been proposed. The most popular are the

models of Lam et al. (1976), Poll et al. (1976), and Yasuda (1985). These models involve a competitive ablation and polymerization (CAP) mechanism which gives an account of the rather complicated and interrelated influences of fragmented elements in the deposition of plasma polymers. It is important to mention that chain-growth polymerization cannot occur under vacuum. This is simply because there are too many chain-carrying species but not enough monomer with a well-defined chemical structure capable of chain-growth polymerization. With the occurrence of fragmentation of the monomer structure, the situation becomes even worse. The way in which a plasma polymer is formed in plasma has been explained by the rapid step-growth polymerization mechanism. The essential elementary reactions are stepwise recombination of reactive species (free radicals) and stepwise addition or intrusion via hydrogen abstraction by impinging free radicals. It is important to recognize that these elementary reactions are essentially oligomerization reactions that do not form polymers by themselves. To form a polymeric deposition, a certain number of steps must be repeated at the surface. As the plasma polymerization proceeds, the activated species may attack the growing polymer layer. This attack can decompose the polymer, extend the cross-linking of the polymer, or cause the elimination of deposited polymer (ablation process). These polymerization and ablation processes proceed competitively, and the overall plasma deposition rate is dependent on the plasma polymerization parameters.

Plasma polymers, noted PP-X (X being the monomer), are not formed by the repetition of a monomer unit like classical polymers. They are disorganized thin films, with short and branched chains (randomly terminated with frequent cross-links) often not reminding the monomers they come from. In terms of material properties, plasma polymers present a great number of advantages when compared to films synthesized, on the one hand by other techniques of vacuum deposition, on the other hand by liquid-route synthesis methods (see article entitled “PECVD”).

The microstructural properties of plasma polymers depend mostly on the parameters of plasma

polymerization and more particularly on the W/FM parameter. In the monomer-sufficient region (low W/FM values), monomer molecules are subjected to less fragmentation to be plasma polymerized, and plasma polymers with less arrangement and small loss of some groups such as hydrogen, methyl, hydroxyl, and carbonyl groups are formed. Under such soft synthesis conditions, plasma polymerization retains more the molecular structure of the monomer; plasma polymers are more organic and less highly cross-linked and thus resemble more conventional polymers; they are said to be polymer-like materials. In the monomer-deficient region (high W/FM values), monomer molecules are subjected to heavier fragmentation, and plasma polymers with much more rearrangements and a larger loss of some groups (especially carbon-based ones) are formed. Under such drastic synthesis conditions, plasma polymers are harder, more inorganic, and more highly cross-linked; they are said to be ceramic-like. For intermediate values of W/FM, a wide range of hybrid materials can be manufactured. Let us consider the case of hexamethyldisiloxane (HMDSO), widely used as monomer in plasma polymerization (Ayril et al. 2008). In soft plasma conditions, the plasma film synthesized from HMDSO has a structure close to those of the HMDSO monomer and also the polydimethylsiloxane (PDMS), which is the closest conventional polymer, as shown by Fourier transform infrared (FTIR) spectroscopy; this plasma film is thus called PDMS-like plasma polymer; its density is quite low, equal to 1.1. In hard plasma conditions, the obtained plasma film is similar to amorphous hydrogenated silica with a density of 2.2; it is noted a-SiO₂:H ("a" for amorphous, ":H" for hydrogenated); the dilution with an oxidative gas as O₂ or N₂O in the plasma reactor can enable to achieve this silica structure at lower W/F values. Mass spectrometry (MS) is a very useful technique to reveal the low fragmentation of the monomer in soft plasma conditions and, on the contrary, the formation of many light species due to strong fragmentation in highly energetic plasmas.

Although considered as dense materials, plasma polymers are characterized by a free

volume comparable to ultramicroporosity (spaces between chains lower than 0.7 nm). Changing the plasma parameters in the preparation of films can enable to tune this free volume as well as the chains flexibility. The approaches that may achieve enhanced free volume and chain flexibility can be summarized as follows: (1) minimization of the W/FM parameter, (2) pulsing of the RF field to reduce the plasma-on time, (3) use of a Faraday cage around the substrate, (4) positioning the sample downstream from the plasma zone (post-discharge configuration), (5) use of monomers containing polymerizable double bonds, and (6) use of a cold substrate. It is possible to further increase the free volume and change it into micro- (pores diameter between 0.7 and 2 nm) or meso- (pores diameter of some nanometers) porosity by adding a porogen in the plasma reactor as comonomer and then eliminating it from the prepared film by thermal or UV posttreatment (Favenec et al. 2004; Rouessac et al. 2006). The porogen approach is mainly applied to polymer-like plasma films. Indeed, ceramic-like plasma materials are usually required for their highly dense structure; nevertheless, they sometimes naturally contain some microporosity because of chain breakings due to very high cross-linking degrees (Roualdes et al. 2002).

For membrane applications, plasma polymerization is usually performed on a highly porous substrate whose only role is to mechanically support the thin plasma polymer, called plasma-polymerized membrane in this case. Nevertheless, plasma polymerization can also be applied on a dense or poorly porous substrate being already an active membrane; in this case, it could achieve the same effect as plasma etching or plasma functionalization (i.e., modification of surface characteristics of the membrane substrate) with additional advantageous characteristic features of the nanometer film of plasma polymer. Moreover, a special kind of plasma polymerization that has received increased attention in recent years is the preparation of plasma polymers by radio-frequency sputtering from polymeric targets. Most attention is paid to fluorocarbon plasma polymer films sputtered from polytetrafluoroethylene (PTFE) using magnetrons

(Finsterwalder and Hambitzer 2001). The main advantage of this innovating process is that the deposition rate and the organization of the chains of the material structure are much higher than in the case of classical plasma polymers. While the activation mechanism is very different from that of the classical plasma polymerization, the deposition mechanism is not.

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Plasma Polymerized Membrane

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Plasma-polymerized membrane names a plasma polymer deposited on a highly porous substrate

(which plays the role of mechanical support) having specific separation properties.

The high degree of flexibility in free volume and chemical structure of plasma-polymerized membrane (see entry “► [Plasma Polymerization](#)”) makes them good candidates as membrane materials. Plasma polymers have been used as membrane materials since the 1980s; the first reported study was from Yasuda (Yasuda 1984). Their main advantages in such an application field are their high cross-linking degree giving them high separation efficiency as well as high chemical and thermal stabilities and their small and easily tunable thickness enabling a modulation of their permeation ability. As plasma polymers are not self-supported, they must be deposited onto symmetric or asymmetric support with a surface pore size and a surface roughness that should be in agreement with the deposited thickness. This support primarily acts as a mechanical support. The plasma polymerization technique cannot deposit thin films on the pore walls inside porous substrates like it can be done by counter diffusion CVD, but plasma polymerization is able to modify the mouth of the pores at the surface of substrates, especially if the latter is macroporous (pores diameter above 50 nm). In that case, the final membrane properties depend both on the plasma polymer and on the starting support as the applied plasma polymerization process duration is not enough to make a complete and homogeneous layer. In the case of a complete homogeneous layer, the transport properties will be mainly governed by the intrinsic separation properties of the plasma polymer.

The first developed plasma-polymerized membranes have been intended to gas permeation or retention (Inagaki and Tsutsumi 1986; Inagaki et al. 1990; Roualdes et al. 2002; Julbe et al. 2008) and also pervaporation; more recently, plasma-polymerized membranes have been prepared for liquid separation processes (nanofiltration and ultrafiltration essentially) (Roualdes et al. 2010). For gas or liquid separation, membranes providing high fluxes of penetrants are required. Polymer-like plasma films are more suitable in this case. If the plasma film does not totally plug the porosity of its support, the

transport properties across the membrane will be controlled by the viscous flow. If the plasma film constitutes a complete homogeneous layer at the surface of its support, the transport properties of the membrane will be mainly governed by the solution diffusion, microporous surface diffusion, or molecular sieving mechanisms inherent to the plasma polymer. Being highly cross-linked in essence, polymer-like plasma materials are generally not as permeable as conventional membranes. In order to enhance their permeability, the easiest solution consists in reducing their thickness, to the detriment of their mechanical stability. Another solution is to increase their free volume and/or chain flexibility to make them resemble more conventional polymers. For gas retention (packaging application essentially), membranes providing low fluxes of penetrants are required. Ceramic-like plasma films are more suitable in this case; their transport properties are rather controlled by the molecular sieve mechanism as for classical crystallized ceramics.

The development of polymer-like plasma films has been more recently applied to fields using ion-conducting membranes such as electromembrane processes (electrodialysis in particular), electrochemical sensors, or, more broadly, the energy production devices (fuel cells, Li-ion batteries, etc.) (Roualdes et al. 2010). Such applications require the use of materials having a good swelling in water and containing specific functions, often charged, distributed in an ordered manner in order to form effective channels of ionic conduction. Obtaining such materials by plasma polymerization is particularly challenging and requires a delicate research task in the choice of the precursor (s) and the adjustment of plasma parameters.

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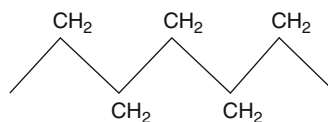
Plasma Polymers (PPs)

Tauqir A. Sherazi

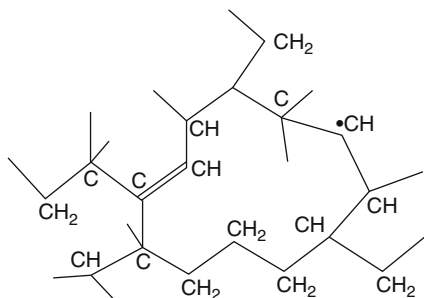
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The term plasma polymer represents a material that is created as a result of a passage of monomer in gaseous form through the glow discharge (Oadian 2004), or simply one should say that an electric discharge in an organic gas produces plasma polymer. Usually, it is deposited in the form of a thin film. Plasma polymers are different from the conventional polymers. In general, conventional polymer has regularly repeating units (Fig. 1), while in the case of plasma polymers, a great number of free radicals are trapped within the network; because of these radicals, the chains are short, and in addition they are randomly branched and terminated with a high degree of cross-linking (Fig. 2).

The application of plasma causes the generation of a great number of free radicals which are trapped within the plasma polymer network. These radicals cannot recombine rapidly, and



Plasma Polymers (PPs), Fig. 1 High density polyethylene (HDPE), an example of conventional polymer



Plasma Polymers (PPs), Fig. 2 Hypothetical structure of a hydrocarbon plasma polymer (Biederman 2004)

therefore when the plasma polymer is exposed to the open atmosphere, they react with the oxygen and water vapor. These free radicals are the cause of often observed aging processes in plasma polymers. Plasma polymers possess a rather disordered structure, and this depends on the intensity and energy of the species bombarding the growing film.

Applications

The advantages of plasma polymer films include excellent coating adhesion on almost all substrates (Feddes et al. 2004), chemical and mechanical stability (Hamerli et al. 2003), thermal stability (Zhang et al. 2003), and high barrier effects (Moffitt et al. 2000). Applications of plasma-polymerized films are associated with biomaterials, textile industry, electronics (e.g., semiconductors, insulators, thin-film dielectrics), optical applications, chemical processing (reverse osmosis membrane, permselective membrane), and surface modification (adhesive improvement, protective coating). A significant area of research has been on the use of plasma polymer films as permeation membranes. The permeability characteristics of plasma polymers deposited on porous substrates are different than usual polymer films. The characteristics depend on the deposition and polymerization mechanism. Plasma polymers as membranes for separation of oxygen and nitrogen, ethanol and water, and water vapor permeation have all been studied (Inagaki 1996). The application of plasma-polymerized

thin films as reverse osmosis membranes has received considerable attention as well (Kim and Kim 2001).

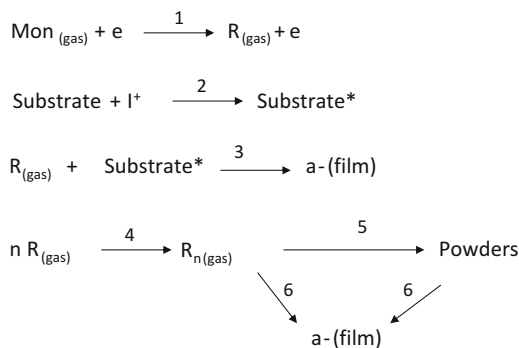
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Plasma-Enhanced Chemical Vapor Deposition

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Plasma-enhanced chemical vapor deposition (PECVD) is a process of film formation onto a substrate when a plasma is applied to a proper vapor or gas precursor. PECVD coatings can be both organic and inorganic, depending on the precursor choice and the experimental conditions used for the deposition. When the deposited film



Plasma-Enhanced Chemical Vapor Deposition, Fig. 1 Sketch of the activated growth model

is organic, the PECVD process is commonly referred to as “plasma polymerization,” and the precursor is termed monomer. However, plasma-deposited films pretty much differ from conventional polymers since their structure has no repeating unit. The layers deposited by PECVD are typically: (i) well adherent, (ii) pine-hole-free, (iii) amorphous and cross-linked, and (iv) conformal and 3D object compatible, (v) with tunable chemical composition and structure. This process allows for the deposition of films with thickness in the range 10–10,000 nm, with deposition rates normally of the order of tens of nm/s and in some cases hundreds of nm/s.

The growth mechanism of PECVD coatings, known as activated growth mechanism (AGM), has been deeply investigated (d’Agostino 1990; Milella et al. 2005; d’Agostino and Palumbo 2012) and is summarized in Fig. 1.

The monomer (*Mon*, step 1) is fragmented in the gas phase by electron impact (see ► [Cold Plasma](#) in this encyclopedia), with the formation of different radicals (*R*). Ion bombardment of the substrate and of the growing film influences the deposition rate since impinging ions transfer energy to the surface, eventually creating surface defect sites (active sites) with reduced activation energies for dissociative chemisorptions (*Substrate**, step 2). Radical species can then adsorb and react with the active sites, thus contributing to film growth (step 3). Bombardment of material surface by low-energy ions can lead to breakage of chemical bonds, surface diffusion,

and heating, which contribute to film densification and to enhanced film-substrate adhesion. Moreover, the energy transfer by impinging ions can favor the molecular dissociative chemisorption. High-energy ion bombardment can determine dramatic rearrangement of the structure of the growing film, such as sputtering of surface atoms, structural damage, and high internal stress. In this extremely reactive scenario, the film grows with a complex and cross-linked structure and with a not conventional chemical composition.

Instead of sticking directly to the surface of the growing polymer, radicals can also polymerize in the gas phase forming oligomers (*R_n*, step 4) or even powders (step 5) which can be afterwards included in the growing film (step 6). However, this second route generally leads to polymers less compact and with poor adhesion to the substrate.

Based on this mechanism it appears quite straightforward that the chemical composition and structure of PECVD films can be finely tuned by properly adjusting process parameters such as input power, pressure, feed composition, substrate temperature, and self-bias (see ► [Cold Plasma](#) in this encyclopedia).

In the field of membrane processing, PECVD can be used both to modify the surface of commercially available membranes and to prepare freestanding ones. These membranes mainly find applications in the field of gas and liquid separation, fuel cells, sensors, and biomaterials (Roualdes et al. 2010; Memoli et al. 2007; De Bartolo et al. 2005).

The gas and liquid permeability of membranes can be tuned with the aid of suitable PECVD coatings, through the control of the surface wettability or inducing specific chemical interactions between the permeant molecules and the film. Silicon oxide-like coatings have been widely exploited as barrier to control gas and vapors permeation (Coclite et al. 2010; Creatore et al. 2001; Julbe et al. 2008). Acid and base functionalized coatings can be deposited on conventional membranes to enhance their liquid or vapor separation performances (Weibel et al. 2007).

PECVD ion exchange membranes can mainly find application for the production of planar

proton exchange membrane fuel cells. Commonly, the membranes are prepared feeding the plasma with an acid precursor and a fluorocarbon monomer. The challenge in this kind of process is to retain in the deposited films the acid functionality, which can be easily cleaved in plasma. This is usually obtained by lowering the energy of the plasma by properly adjusting process parameters. Proton conductivities in the range of 10^{-3} –2 mS/cm have been reported; however, values as high as 180 mS/cm have been recently achieved (Brault et al. 2006; Thery et al. 2010).

Polyethersulfone (PES) membranes have been coated with plasma-polymerized acrylic acid for the subsequent immobilization of galactonic acid through a hydrophilic spacer arm molecule. This strategy allowed the setup of a bioreactor for biomimicking the cellular microenvironment accomplishing long-term maintenance and differentiation of human hepatocytes (Memoli et al. 2007; De Bartolo et al. 2005).

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Plasma-Enhanced Chemical Vapor Deposition (Plasma Polymerization)

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P

PECVD is the main effect caused by the interaction between a cold plasma (defined in the article entitled “Vapor Plasma Membrane Treatment”) and a material placed within it, in the case of condensable gases (organic, inorganic, or organometallic compounds) used as gaseous phases. PECVD is due to recombination of the reactive species adsorbed on the surface of the substrate and results in the formation, on the surface of the substrate, of a deposit made up of a three-dimensional matrix formed from fragments of the reagent gas combined in a random way.

The PECVD process is mainly used for the preparation of inorganic, hybrid, or polymer-like thin layers. In the field of membranes, most of the plasma deposits are prepared from organic precursors; in that case, one calls the deposition

process plasma polymerization preferentially to PECVD. Among the numerous PECVD parameters, the ones having a direct effect on the fragmentation of the precursor are logically the most influent. Three parameters have a particularly pronounced effect: the nature of the precursor represented by its molecular weight M , the power of the electric discharge W , and the precursor flow rate F . The energy-input level manifested by W/FM (given in units of J/kg, or energy per mass of monomer), introduced by Yasuda (1985), is the predominantly important factor determining the extent of fragmentation. Low W/FM values are related to operating conditions where the activated species have a far lower concentration than precursor molecules introduced into the plasma; in such a range of W/FM values, called precursor sufficient region, the number of activated species, and consequently the plasma film deposition rate, increases with W/FM . For medium W/FM values, corresponding to the competition region, the quantity of precursor molecules introduced into the plasma is exactly the quantity likely to be activated; in that case, the film deposition rate is invariable as a function of W/FM . For high values of W/FM , corresponding to the precursor deficient region, the material deposition rate decreases with W/FM because of the lack of precursor molecules likely to be activated.

Plasma deposits are disorganized thin films, with short and branched chains (randomly terminated with frequent cross-links) often not reminding the precursor(s) they come from. In terms of material properties, plasma deposits present a great number of advantages when compared to films synthesized, on the one hand, by other techniques of vacuum deposition, and, on the other hand, by liquid-route synthesis methods:

- Like all the vacuum deposition techniques, PECVD makes it possible to work out very thin films with thicknesses of a few nanometers to a few microns, which is impossible with liquid-route synthesis methods. The deposition rate can be high (several $\mu\text{m min}^{-1}$) (Storgaard-Larsen and Leistiko 1997) making the process ideal for industrial applications.

- One of the major interests of this technique is the possibility of depositing materials at ambient temperature on substrates sensitive to heat such as conventional organic polymers (which is not possible with conventional chemical vapor deposition (CVD): chemical plating in pyrolytic phase vapor). The polymeric supports constitute, with glasses, semiconductors, ceramics, and metal surfaces, the large variety of substrates on which the plasma deposits have a good adherence.
- The materials deposited by PECVD are generally dense, amorphous, strongly cross-linked, and present a low density of defects and holes compared with those obtained by the other vacuum deposition techniques such as evaporation or sputtering.
- The three-dimensional and highly cross-linked structure of the plasma deposits is at the origin of a number of very specific properties of these materials, properties that one does not find in their counterparts worked out by conventional ways: chemical inertia, good thermal stability, anticorrosive character, and barrier properties with respect to oxygen and water vapor in particular.
- PECVD makes it possible to adjust the chemical composition and the microstructure of deposited materials and thus to modify the physical and chemical properties of these materials by the simple variation of the parameters of the process, and this in a field much broader than the other deposition techniques. If, from a technological point of view, this requires a rigorous control of the parameters of the process, the complexity and variety of active species and reaction steps directly related to the plasma parameters offer a high degree of flexibility in prepared materials properties.

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Plastron Effect

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Plastron, meaning shielding, was first used in 1910 by zoologist, F. Brocher, referring to a layer of gas adhering closely to the body surface between the hairs of underwater Coleoptera family (Brocher 1909). This air layer serves as an air supply for a variety of arthropods while performing living activities underwater. A well-known example is the water spider (*Argyroneta aquatica*), which spends its entire life living underwater (Fig. 1). The hairy structure of the water spider is thus necessary not only to lower the contact area with the water surface but to enable them to breathe when submerged. This activity is consequently termed *plastron respiration*. The gases, oxygen and carbon dioxide, are supplied and removed through the diffusion across the bubble surface from the ambient water. The air layer is maintained by an array of hair with their tips forming pillars lying roughly parallel to the body. The curvature pressure and the mechanical strength of hairs sustain the interface, while higher ambient hydraulic



Plastron Effect, Fig. 1 Air clinging to the hydrophobic hairs on the abdomen of a spider away from the diving bell (Seymour and Hetz 2011)

pressure may buckle the hairs causing the collapse of the plastron air. Earlier observations found that the collapsing point for most insects occurs in the pressure between 1 and 5 atm (Thorpe and Crisp 1947). With more sophisticated imaging equipment, calculations, however, estimated that the hairs should be stable at a pressure up to 40 atm (Hinton 1976).

Nowadays plastron is commonly used to describe the thin air layer trapped on submerged surfaces in Cassie-Baxter state. The air layer trapped by the superhydrophobic surface is thermodynamically unstable. Except for a few species that actively maintain the trapped air for breathing the air dissolves into the water. The lotus leaf loses its plastron air within an hour when immersed to the depth of half meter. The metastable underwater superhydrophobicity limits its potential applications, such as drag reduction or anticorrosion. The lifetime of plastron is controlled by the mass flux of air into water and is driven by partial gas pressure difference between the interface. The decay of plastron generally has two distinct phases. At the initial phase, air diffuses into water through the planar interface, and its mass flux shows exponential depth dependence. With further thinning to a critical thickness, the plastron forms into spherical cup-shaped air bubbles resulting in a rapid decay driven by the Laplace pressure (Poetes et al. 2010). The lifetime of plastron varies with its surface energy and topography, while detailed studies are still very limited to date.

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Plate and Frame Membrane

► Plate and Frame Membrane Module

Plate and Frame Membrane Module

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Synonyms

Plate and frame membrane; Plate and frame module

The plate and frame module design provides a configuration which is closest to the flat membranes used in the laboratory (Mulder 1997).

The most important elements of the module construction are (Blackmer and Hedman 1979):

- Flat membrane
- Membrane supporting plate/spacer
- Feed distribution plate

In a plate-and-frame module configuration (Fig. 1), sets of two membranes are placed in a sandwich-like fashion with their feed sides facing each other. In each feed and permeate compartment, a suitable spacer is placed. A plate-and-frame stack is build up by the number of membrane sets needed for a given membrane

area equipped with sealing rings and two end plates. The packing density (membrane surface per module volume) of such modules is low and about 100–400 m²/m³ (Mulder 1997).

A schematic flow path in a plate-and-frame module is illustrated in Fig. 2. In order to reduce channeling (tendency to by-pass parts of the membrane along a short cut) and to establish a uniform flow distribution, baffles have been introduced (Mulder 1997).

The advantages of plate-and-frame modules are the following (Blackmer and Hedman 1979):

- Exchange ability of single membranes
- Low sensitivity to particulate blocking of the feed channels
- Usage of flat membranes without the usage of glue

The disadvantages are the following:

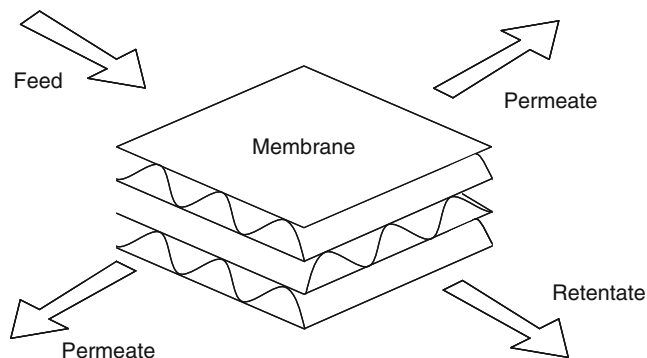
- Need of several sealings
- Pressure drop
- Low packing density

Plate-and-frame modules were the earliest version of membrane modules (Mulder 1997; Baker 2004) and are today still used in ultrafiltration and pervaporation processes. There is only one plate-and-frame configuration used in solution-diffusion membranes (Ohlrogge and Ebert 2006). This design may be relevant in the future for flat perovskite membranes (Etchegoyen et al. 2006; Melin and Rautenbach 2007; Kondo 1992).

Plate and Frame

Membrane Module,

Fig. 1 Drawing of a plate-and-frame module taken from Scholz et al. (2011)



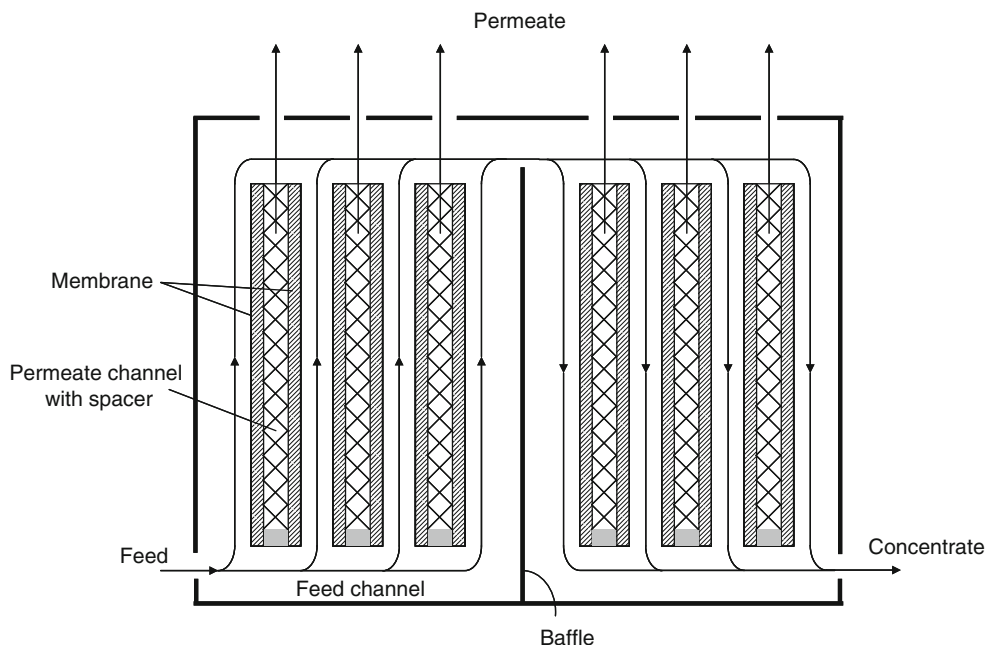


Plate and Frame Membrane Module, Fig. 2 Schematic flow path in plate-and-frame-module taken from Scholz et al. (2011)

The plate-and-frame module is highly effective in pervaporation applications, but is much less popular than spiral wound and hollow fiber modules for gas separation applications due to the lower membrane area per unit volume that can be accommodated (Baker et al. 1991). The only commercial application for a plate-and-frame device in gas separation is the oxygen enrichment from air for small-scale medical applications (Lemanski and Lipscomb 2001; Bao and Lipscomb 2002) and for organic vapor recovery as commercialized by Borsig, with a special custom design envelope-type gas separation module (Scholz et al. 2011; Melin and Rautenbach 2007).

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Plate and Frame Module

- [Cross-Flow Membrane Module](#)
- [Plate and Frame Membrane Module](#)

Platinum

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Platinum

Platinum (Pt) is a chemical element with an atomic number of 78 and atomic mass of 195.09 (Platinum (Pt) 2012).

General Facts

Platinum has five naturally occurring stable isotopes and one naturally occurring radioactive isotope (Pt 190) that decays with a half-life of 6.5×10^{11} years. There are also a few known synthetic isotopes. Platinum is a silver-white metallic element. Platinum is a relatively rare and usually occurs in combination with other metals including iridium, osmium, or nickel. South Africa is the dominant supplier of Pt which accounts for approximately 80 % of the world production. The world's most important deposits occur in the North West Province of South Africa near Rustenburg and Brits.

Platinum is one of the six metallic elements forming the so-called PGM (platinum-group metals): ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). These elements are all transition metals clustering in the groups of 8, 9, and 10 and periods 5 and 6 in the periodic table.

Platinum has a melting point of 1,769 °C (Platinum (Pt) 2012) and density of 21.45 g/cm³ at 20 °C. It has a face-centered cubic crystal structure.

Use of Platinum

Platinum is used as a catalyst in the chemical industry (e.g., in sulfuric acid production,

petrochemistry) and in catalytic converters in the automotive industry. It is also used to make electrical components, corrosion-resistant chemical laboratory equipment, and jewelry. Platinum is also used in many medical applications (electrodes, dentistry, as a component for certain types of anticancer drugs, etc.). One of the potentially large applications for platinum and platinum-based alloys is its use in fuel cells as a catalyst.

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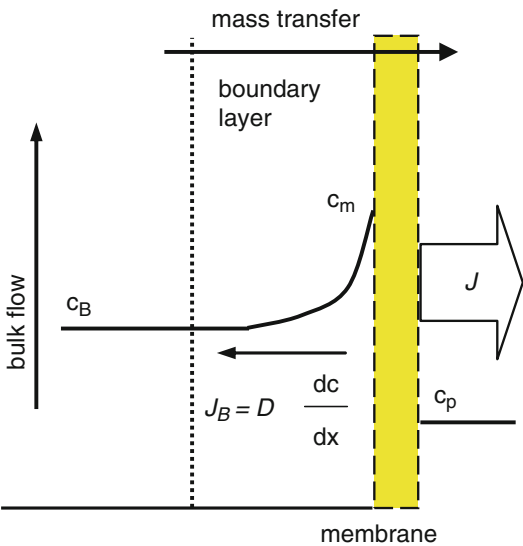
Polarization in Membrane Operations

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Polarization phenomena are inherent to all membrane separation processes. Since a membrane has the ability to transfer one component of a mixture more readily than others or to retain solutes completely, the rejected substances are gradually accumulated at the membrane surface, whereas a solvent permeates freely through the membrane. This leads to the formation of a boundary layer adjacent to the membrane, where the concentration of the retained solutes is higher than in a bulk solution (Fig. 1). This difference in the concentration of solutes is termed as **concentration polarization (CP)**. The CP phenomenon causes a serious problem in every membrane process because it reduces the driving force of the mass transfer and thus leads to a decrease in the permeate flux.

The extent of CP strongly depends on the type of membrane process, its driving force, and the feed



Polarization in Membrane Operations, Fig. 1 Concentration polarization. Concentration profile under steady-state conditions

composition. The **CP** effect is most severe when a permeate flux is high and the mass transfer coefficients (and diffusion coefficients) of the separated species are low (Table 1). Thus, the **CP** is especially severe in the case of pressure driven membrane techniques, such as microfiltration (MF) and ultrafiltration (UF), which are applied to separate the macromolecular solutes, small particles, colloids, and emulsions. The concentration of the accumulated molecules might be so high that a gel layer can be formed on a membrane, which induces an additional resistance to the mass transfer on the feed side.

In reverse osmosis (RO), an increase of salt concentration in the boundary layer can increase the osmotic pressure and reduce the driving force. The severity of **CP** in RO is lower than in MF or UF because the permeate flux is lower and the mass transfer coefficients of salts are high. However, an increase of salt concentration in the layer adjacent to the membrane results in their precipitation onto the membrane surface (scaling), which contributes to a decrease of permeate flux (Mulder 1991).

Scaling is also a serious problem in nanofiltration (NF). The **CP** in NF causes a reduction of a permeate flux mainly due to an increase

Polarization in Membrane Operations, Table 1 Effects of polarization concentration in various membrane operations (based on Mulder 1991)

Membrane operation	CP influence	Mass transfer coefficient/diffusion coefficient	Permeate flux
Reverse osmosis	Moderate	Large / $10^{-9} \text{ m}^2/\text{s}$	Small/moderate
Nanofiltration	Moderate	Large	Moderate
Ultrafiltration	Strong	Small/ 10^{-10} to $10^{-11} \text{ m}^2/\text{s}$	Large
Microfiltration	Strong	Small/ 10^{-10} to $10^{-11} \text{ m}^2/\text{s}$	Large
Gas separation	Very low	Large/ 10^{-4} to $10^{-5} \text{ m}^2/\text{s}$	Small
Pervaporation	Low	Large	Small
Electrodialysis	Strong		
Dialysis	Low	Large/ $10^{-9} \text{ m}^2/\text{s}$	Small
Membrane distillation ^a	Low	Large	Small/moderate

^aStrong influence of temperature polarization

of osmotic pressure of the retained salts. Moreover, similarly as in UF and MF, the accumulated organic molecules can form a gel layer (fouling or biofouling) (Schafer et al. 2005).

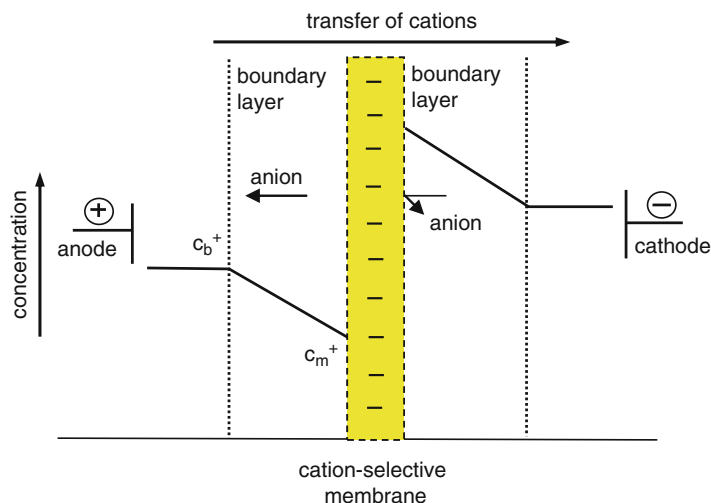
The concentration polarization also strongly limits the efficiency of electrodialysis (ED). The transport of charged molecules is the result of an electrical potential difference (driving force) through an ion-selective membrane. Cations are driven to cathode and anions to anode. For example, through a cation-selective membrane only cations can be transferred at the potential difference. However, the transfer across the membrane is faster than in boundary layers on both sides of the membrane. Thus, the concentration of cations will be lower at the membrane surface on the anode side and higher at the membrane surface on the cathode side (Fig. 2). Thus, **CP** appears on both sides of the membrane. Moreover, a diffusive flow occurs in the boundary layers (Mulder 1991).

The effect of **CP** on the membrane processes such as gas separation, pervaporation, and dialysis is low or very low (Table 1).

Polarization in Membrane

Operations,

Fig. 2 Concentration polarization in electrodialysis in the presence of cation-selective membrane



In the case when a hydrophobic membrane separates two solutions of different temperature as in membrane distillation (MD), the temperature and concentration polarization phenomena occur. In MD, only volatile components are transferred through a hydrophobic, porous membrane. Therefore, the energy required for water evaporation is supplied from hot feed solution on the liquid-membrane interface. As a result the local temperature in the boundary layer is gradually decreasing. On the cold side, the water vapor is condensed and energy (latent heat) is released, therefore, the temperature in the boundary layer increases. For this reason, the temperature of the liquid-membrane interface on both sides of the membrane is different from that in bulk solutions. This difference is referred to as **temperature polarization**. Additionally, an accumulation of solutes on the feed side leads to the concentration polarization.

The extent of **CP** can be reduced by increasing flow rate of the stream over a membrane, application of permeate pulsing, operation below a critical flux, or using an ultrasound system (Schafer et al. 2005).

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Polyacetylene-Based Membrane Materials

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Many of disubstituted polyacetylenes are glassy polymers distinguished by extremely high gas permeability. The first polymer of this class poly(trimethylsilyl propyne) (PTMSP) was discovered by Masuda et al. (1983). All these polymers have very rigid main chains so the glass transition temperature is, as a rule, above the onset of thermal decomposition. PTMSP due to the bulky SiMe_3 side group has extremely large gas permeability coefficients (e.g., $P(\text{O}_2) = 6000$ Barrer): until very recently, it was considered as the most permeable polymer among all known. Recently, it was shown that other polyacetylenes reveal even higher gas permeability (Hu et al. 2008). Several structural analogs of PTMSP [poly(trimethylgermyl propyne) (PTMGP) and poly(methyl pentyne) (PMP)] also reveal high permeability. Many other disubstituted polyacetylenes have been prepared; they show a wide range of gas permeability (Nagai et al. 2001). Due to the trade-off between permeability and permselectivity, the most permeable polyacetylenes

are low selective materials. PTMSP is characterized by a large free volume as has been shown by positron annihilation lifetime spectroscopy (PALS). An unusual feature of PTMSP and other highly permeable polyacetylenes is a negative activation energy of permeation, that is, the permeability coefficients increase when temperature decreases. In contrast to conventional glassy polymers, PTMSP and its structural analogs reveal solubility-controlled selectivity in separation of hydrocarbons: the permeability coefficients are larger for higher gaseous hydrocarbons (e.g., n-butane) as compared to the permeability coefficient of methane (Pinnau and Toy 1996). This important feature makes them suitable membrane materials for separation of hydrocarbons of natural and associated petroleum gases. A disadvantage of highly permeable polyacetylenes is their tendency to aging, that is, a reduction of permeability in time. The rate of this process is especially high for PTMSP: for some samples, permeability decreases by a factor of 100 during 2 months of exploitation. This can be the main factor preventing practical applicability of highly permeable polyacetylenes in membranes. PTMSP and its structural analogs include double bonds in the main chains, so different cis-trans-configurations can be realized depending on the selection of a catalyst and polymerization conditions. The polymers with prevailing cis- or trans-configuration have somewhat different properties: solubility in various organic solvents, permeability coefficients, and tendency to aging. Since polyacetylenes are soluble in different organic solvents, composite membranes can be prepared from them. Thanks to the high permeability of these polymers, laboratory-scale membranes with very high permeance (say, 20–30 m³(STP)/m² h/bar) have been prepared and tested in different separation processes. It has been also reported that PTMSP can form good and permeable organophilic pervaporation and nanofiltration membranes (Volkov et al. 2009, 2013).

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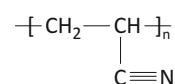
Polyacrylonitrile (PAN)

Alexey Volkov

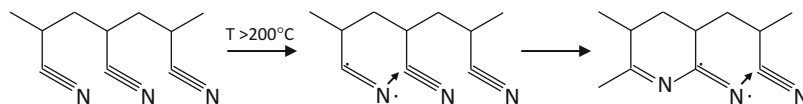
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Polyacrylonitrile (PAN) is semicrystalline thermoplastic polymer (see Fig. 1 for structural formula of PAN), which is synthesized by radical polymerization in the presence of conventional initiators, for example, peroxides. There are six different technologies of production of monomer, acrylonitrile: (a) from ethylene via ethylene oxide and ethylene cyanohydrins, (b) oxidative ammonolysis of propylene or propane, (c) from acetylene and hydrocyanic acid, (d) from ethylene via acetaldehyde and hydroxynitrile, (e) from propylene and nitrogen oxide, and (f) from ethylene, hydrocyanic acid, and oxygen. PAN has a good resistance in a wide range of organic solvents:

Polyacrylonitrile (PAN),
Fig. 1 Structural formula
of polyacrylonitrile



Polyacrylonitrile (PAN),
Fig. 2 Radical mechanism
 of polyacrylonitrile
 cyclization



insoluble in hydrocarbons, chlorinated hydrocarbons, ketones, diethyl ether, and acetonitrile (Mark 2009). Major application of PAN is textile fibers.

When homopolymer PAN is heated above 180–200 °C, the autocatalytic reaction of cyclization takes place through a free radical mechanism (see Fig. 2). Further heat treatment leads to carbonization of initial material. PAN-based fibers are the main raw material for carbon fiber production. Polymer softening temperature is close to the one at which cyclization starts; therefore, PAN can be only processed to fibers by dry or wet spinning. Besides homopolymer, PAN copolymers can be used in order to improve carbon fiber quality. Carbon fibers have a number of advantages like low density, high stiffness, good chemical and temperature resistance. As a result carbon fibers are widely used in production of novel lightweight composite materials with high mechanical properties for different applications like aerospace industry, machinery and military applications, sports, and other applications (Gupta et al. 1991).

Different copolymers of acrylonitrile offer a large family of materials for different applications. Acrylonitrile-butadiene rubber with acrylonitrile content from 20 % to 50 % is known as nitrile rubber that has high oil and abrasion resistance. Copolymer of acrylonitrile with butadiene and styrene is a famous ABS plastic that is extensively used in different applications such as the automotive industry (e.g., bumpers), different plastic carcass, parts, and goods. Acrylonitrile and butadiene provide good hardness, while incorporated rubbery particles offer shock absorbance that makes this material less brittle. In addition, polar groups of acrylonitrile also provide interchain bonding to improve mechanical properties and good dimension stability. ABS has good chemical stability and low water adsorption and can be operated at low and high temperatures. ABS can be processed with standard methods (Rosato et al. 2000).

PAN has been widely used as a membrane material. Regarding transport properties, PAN belongs to the group of extra low permeable (barrier) polymers (e.g., $P(\text{CO}_2) \sim 10$ Barrer). Due to high chemical stability, PAN is used for fabrication of micro- and ultrafiltration membranes both for aqueous and nonaqueous applications. These flat membranes are fabricated on a nonwoven by a phase inversion process. It is worth to mention, that PAN ultrafiltration membranes are attractive for use as an efficient porous support for fabrication of thin film composite membranes for gas and vapor separations, pervaporation and organic solvent nanofiltration. Several companies have manufactured thin film composite membranes based on PAN porous supports over the years.

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Polyacrylonitrile Membrane

George Dibrov

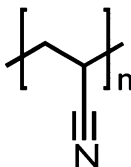
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The majority of commercial methods of production of polyacrylonitrile (PAN) are based on free radical polymerization of acrylonitrile (Fig. 1).

Chemical and physical properties of PAN (Andrady 1999, Scharnagl and Buschatz 2001):

Polyacrylonitrile

Membrane, Fig. 1 The chemical structure of the polyacrylonitrile repeat unit



- Melting point: 317 °C
- Glass transition temperature: 87–125 °C
- Decomposition temperature: >250 °C
- Density: 1.17 g/cm³
- Solubility: DMF, DMSO, DMAc, NMP, dioxanone, chloroacetonitrile, dimethyl phosphite, dimethyl sulfone, ethylene carbonate, γ-butyrolactone, conc. sulfuric and nitric acid, and conc. salt solutions of LiBr or NaCNS in water
- Water uptake: 1–2.4 % (25 °C, 65 % rel. humidity)
- Good resistance against mineral acids and weak alkaline solutions, moderate against strong alkalines
- Permeability coefficient $P(\text{m}^3(\text{STP}) \cdot \text{m} \cdot (\text{s} \cdot \text{m}^2 \cdot \text{Pa})^{-1} \cdot 10^9)$ of unplasticized film at 25 °C: $P(\text{O}_2) = 0.00015$, $P(\text{CO}_2) = 0.00060$, $P(\text{H}_2\text{O}) = 230$

PAN membranes have attracted much attention due to a variety of excellent characteristics, which include thermal stability and tolerance to most solvents, atmosphere, bacteria, and photo irradiation. Therefore, their exploitation also covers many fields in micro- and ultrafiltration, pervaporation, nanofiltration, reverse osmosis like water treatment, enzyme immobilization, hemodialysis, concentration of whey or protein, concentration of oil/water mixtures, etc. PAN membranes demonstrate high stability against chemical cleaning agents and resistance to sodium hypochlorite, citric acid, weak alkaline solutions, hydrolysis, and oxidation. PAN is highly crystalline and relatively hydrophilic (calc. surface tension is 44 dynes/cm) and is usually copolymerized with more hydrophilic monomers to improve processability and to make it less brittle.

Preparation of PAN membranes is possible by phase inversion from its solutions. PAN membranes for ultra- and microfiltration are developed by GKSS (Scharnagl and Buschatz 2001).

Different membrane morphologies varying from large finger-like pores to homogeneous microporous structures can be obtained. The change from the finger-like pores to globular ones enhances the pressure stability of membranes, which is favorable to the use of membranes as supporting material for composite membranes.

The flux of the membranes can be adjusted between 100 up to nearly 2000 l · (m² · h · bar)⁻¹ with high rejection. By varying the formation parameters, a wide spectrum of membranes with different average pore diameters ($d_{50} = 2\text{--}70$ nm) can be produced. PAN membranes are used in a plate-and-frame module developed in the GKSS research center and now sold by Amafiliter. This module is applicable to nano-, ultra-, and microfiltration and also appropriate for high values of suspended solids. For water reuse, the PAN membranes are also used in Rochem FM-modules.

Microza[®] hollow fiber ultrafiltration modules produced by Pall Corporation feature unique double-skinned polyacrylonitrile (PAN) membranes with dense internal layer. The modules are used in a range of pharmaceutical applications especially in purification and processing of aqueous enzymes and protein solutions, raw water pretreatment to pharmaceutical water purification plant. UF membranes from PAN and its copolymers are also produced by Millipore and Applied Membranes Inc.

PAN can be chemically cross-linked with and without the change in the porous structure of the membrane (Nunes and Peinemann 2001). The surface of PAN membranes can be modified by plasma or conversion of nitrile groups (Ulbricht 2006).

Cross-References

- [Plasma Functionalization](#)
- [Polyacrylonitrile \(PAN\)](#)

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Polyamide (PA)

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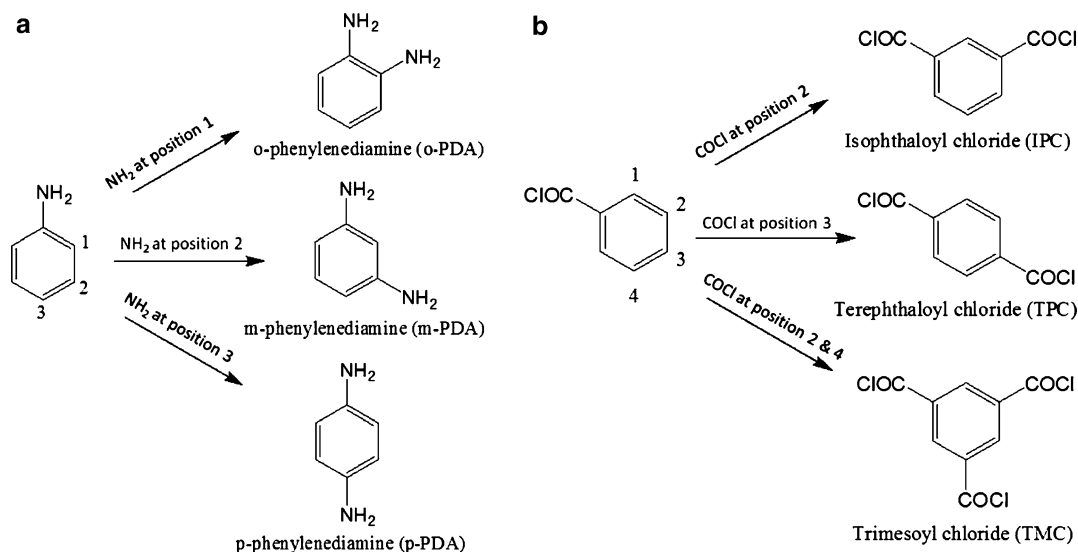
Polyamide (PA) is a polymer where the monomer units are connected together by amide group ($-C(=O)-NH-$). It can be easily synthesized by interfacial polymerization (IP) between polyfunctional amine monomer and polyacyl chloride monomer at the interface between two immiscible solvents with hydrochloride acid (HCl) created as by-product. The concept of IP was first introduced by Morgan in the 1960s (Morgan 1965). The contribution of IP technique to the development of membrane science and technology is so significant, making it almost equivalent to the historical announcement of Loeb-Sourirajan asymmetric membrane prepared from phase inversion technique. By employing this IP technique, an ultrathin, selective PA layer (with thickness between 100 and 500 nm) is able to form over the surface of microporous support membrane, producing a thin-film composite (TFC) membrane with a very good combination of water flux and solute rejection.

Conventionally, interfacially polymerized PA layer is established by immersing support membrane in an aqueous solution containing amine monomer (with concentration mostly between 0.1 % and 1 % w/v), followed by organic solution of acyl chloride monomer (mostly between 0.05 and 0.2 % w/v) which is immiscible with the first aqueous solution (Lau and Ismail 2011). The membrane is then subject to heat treatment process at temperature in the range of 70–90 °C to densify the polymerization properties of PA layer.

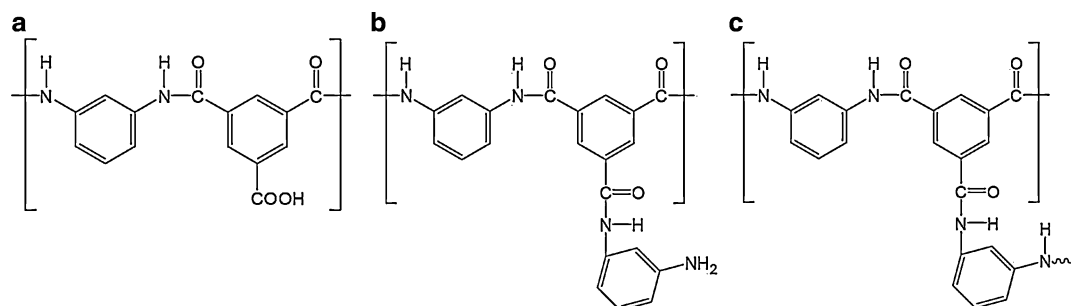
The sequence of immersion process however can be reversed if the support membrane is relatively hydrophobic in nature (Wu et al. 2010). It is mainly because hydrophobic substrate can be well contacted with organic solution of acyl chloride monomer, leading to higher degree of cross-linked PA layer. It has also been reported that the unreacted acid chloride groups on the surface of PA layer could be further reacted by placing the membrane in aqueous solution of amine monomer for second time after the conventional IP approach (Zou et al. 2010). The modified approach is reported to yield membrane surface with larger amount of amino groups ($-NH_2$), causing the membrane to have better antifouling properties than that of membrane prepared from conventional IP approach.

Characteristics of PA are varied depending on the type of amine and acyl chloride monomers selected during IP process (Lau et al. 2012). Figure 1 shows the most frequently used aromatic diamine monomer and bi-/tri-acyl chloride monomers in preparing cross-linked aromatic PA layer. The degree of PA cross-linking depends on not only the organic structure of the monomers used but also factors such as concentration of active reactant in aqueous/organic solution, type of hydrocarbon solvent, reaction time, presence of additive/surface, etc. Figure 2 shows the possible PA structures formed from the reaction of *m*-phenylenediamine (MPD) with trimesoyl chloride (TMC). It is generally agreed that the poly (MPD-TMC) chain is to contain both the cross-linked structure and non-cross-linked (i.e., linear) structure. The carboxylic acid functional group ($-COOH$) arises due to the partial hydrolysis of the acyl chloride unit of TMC during IP. In order to grasp the cross-linking reaction rate of the PA formed, characterizations using Fourier transform infrared (FTIR) spectrometer and X-ray photoelectron spectra (XPS) are generally performed.

However, it must be pointed out that PA is very susceptible to free chlorine attack, causing it to lose its integrity. By exposing PA to chlorine solution, several chemical changes in PA have been proposed. These include (a) chlorination of N–H group of diamine to form N–Cl group, (b) Orton rearrangement – initial chlorination of



Polyamide (PA), Fig. 1 Organic structures of (a) aromatic diamine monomer and (b) bi-/tri-acyl chloride monomer used in synthesizing polyamide



Polyamide (PA), Fig. 2 Possible chemical structures of polyamide prepared from MPD and TMC, (a) linear structure with a pendant COOH group from the hydrolysis

of COCl , (b) cross-linked with a pendant NH_2 group and (c) totally cross-linked polymer chain

the N–H group followed by rearrangement of chlorine to aromatic ring of diamine unit, and (c) direct chlorination of aromatic ring of the diamine unit (Buch et al. 2008). Although PA in nature has low chlorine resistance, the recent research activities in utilizing new types of monomers such as melamine (Han 2013), m-phenylenediamine-4-methyl (MMPD) (Yu et al. 2009), N,N'-dimethyl-m-phenylenediamine (N,N'-DMMPD) (Shintani et al. 2009), and 1,3-cyclohexanebis(methylamine) (CHMA) (Buch et al. 2008) have improved the stability of PA against chlorine stability to a certain extent depending on the

concentration of chlorine solution and exposure period.

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Polyamide Membrane

W. J. Lau

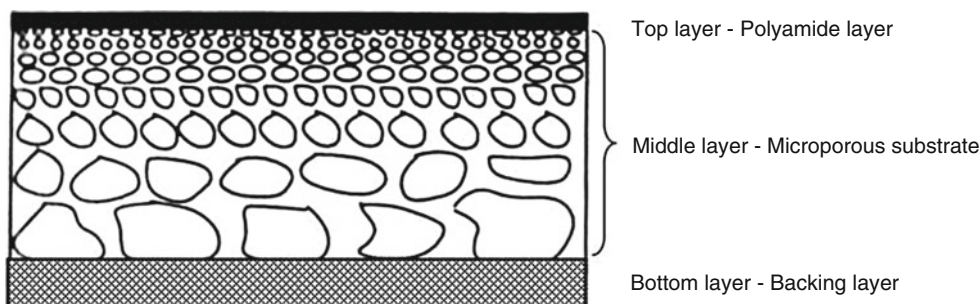
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Thin film composite (TFC) polyamide (PA) nanofiltration (NF) and reverse osmosis

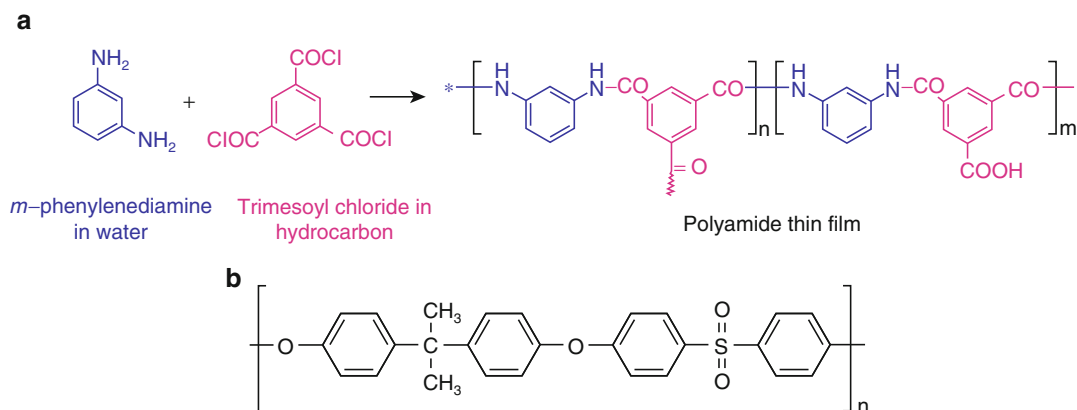
(RO) membranes have been widely applied in many industrial applications such as water purification, wastewater treatment, desalination, food processing, and bio-separation, owing to its right combination of water flux and rejection compared to the typical asymmetric membranes.

Typical TFC PA membrane consists of three different layers made of different materials. Figure 1 illustrates the cross-sectional view of a PA membrane with top thin active layer made of cross-linked PA synthesized on a microporous substrate supported by a backing layer. The top active layer is prepared via interfacial polymerization technique, while the microporous substrate is commonly fabricated through a dry-wet phase inversion technique. The combined fabrication techniques offer distinct advantages as either active layer or substrate can be independently optimized to achieve desirable membrane properties such as high flux/high rejection and greater mechanical strength and compression resistance (Lau and Ismail 2009).

Figure 2 shows the two commonly used active monomers in preparing thin active layer of PA membrane together with the polymer used in microporous substrate preparation. In order to establish a very thin PA active layer on top of a substrate membrane, the substrate is first immersed into an aqueous solution consisting of amine monomer followed by immersion in second hydrocarbon solution of acyl chloride monomer. The membrane is then subject to heat treatment process to densify the polymerization properties of PA layer and/or enhance adhesion of PA thin layer to surface of substrate membrane. The

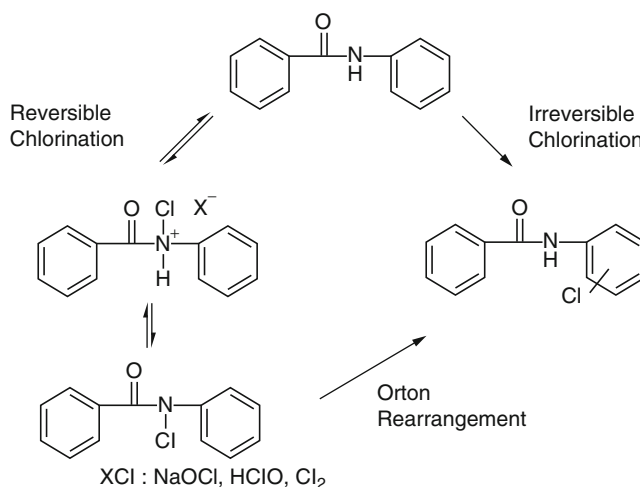


Polyamide Membrane, Fig. 1 Schematic diagram of typical thin film PA membrane made of different three different layers



Polyamide Membrane, Fig. 2 Organic structure of polymer used in thin film PA membrane preparation, (a) top active PA layer synthesized by interfacial polymerization between *m*-phenylenediamine (MPD) in water and trimesoyl chloride (TMC) in hydrocarbon solution and (b) polysulfone (PSf) for microporous substrate preparation

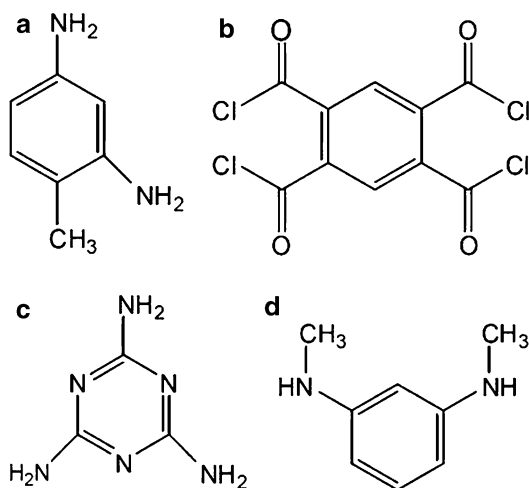
Polyamide Membrane, Fig. 3 The change in the characteristics of PA layer as a result of Orton rearrangement caused by the interaction between an aromatic amide and active chlorine (Kawaguchi and Tamura 1984)



chemical and physical characteristics of the interfacially formed PA film are strongly dependent on a number of important variables. These include type of monomer, concentration of monomer, partition coefficient of monomer, type of hydrocarbon solvent, overall kinetics and diffusion rates of monomer, reaction time, presence of additive/surfactant, posttreatment of the resulting interfacial PA film, etc. (Petersen 1993; Lau et al. 2012). All these variables listed should be taken into consideration during PA membrane fabrication as they play important role in PA layer formation which governs the performance

properties of membranes with respect to permeability/selectivity, fouling resistance, and chlorine tolerance.

A key limitation to typical PA membrane is its poor resistance to continual exposure to chlorine – one of the common disinfectants used in water and wastewater treatment, even at few ppb of chlorine. The changes in chemical and physical nature of PA layer upon chlorine exposure are identified as the main reason causing the membrane performance degradation, shortening membrane lifespan (Misdan et al. 2012). It is reported that the presence chlorine in water is



Polyamide Membrane, Fig. 4 Organic structure of advanced active monomer in preparing chlorine-resistant PA membrane, (a) m-phenylenediamine-4-methyl (MMPD) (Yu et al. 2009), (b) 1,2,4,5-benzene tetracarbonyl chloride (BTC) (Hong et al. 2013), (c) melamine (Han 2013), and (d) *N,N'*-dimethyl-m-phenylenediamine (*N,N'*-DMMPD) (Shintani et al. 2007, 2009)

able to attack the PA structure by forming N-chlorinated amide in the initial step of chlorination process. The process is followed by an irreversible reaction, i.e., ring chlorination through intramolecular rearrangement of chlorine atom into aromatic ring of the diamine moiety via Orton rearrangement as illustrated in Fig. 3 (Kawaguchi and Tamura 1984). Usually, the degree of membrane degradation following the chlorine attack is strongly dependent on the chlorine concentration and the membrane exposure time in feed water which can be expressed as ppm-h. To overcome the limitation of PA membrane without sacrificing its excellent water permeability and selectivity, many attempts have been made over the past several years to develop chlorine-resistant membrane with the use of novel advanced monomers in which some of the research works published have shown promising results in improving membrane stability against chlorine exposure. Figure 4 shows the potential monomers that have been used in improving membrane chlorine resistance. The PA membrane prepared from these monomers in general showed greater or much higher chlorine resistance than the commercial PA membranes.

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Polydimethylsiloxane (PDMS)

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Polydimethylsiloxane (PDMS) is the most known organosilicon rubbery polymer and its glass transition temperature is about -150°C . PDMS, often referred to as “silicone rubber,” can be polymerized from different monomers by hydrolysis

$$\left[\begin{array}{c} \text{CH}_3 \\ | \\ -\text{Si}-\text{O}- \\ | \\ \text{CH}_3 \end{array} \right]_n$$

PDMS is used as adhesive material, particularly, pressure-sensitive materials. Due to good dielectric properties, PDMS is also used for dielectric encapsulation. PDMS is extensively utilized as a polymer matrix for further incorporation of different kinds of

PDMS exhibits the highest values of gas and vapor permeabilities among rubbery polymers. By this reason, it has been extensively studied as a membrane material for different applications, namely, gas and vapor separation (Freeman et al. 2006), organophilic pervaporation (e.g., bioalcohols recovery from fermentation broth) (Vane 2005), and organic solvent nanofiltration (Volkov et al. 2008). PDMS can be used to fabricate hollow fiber, tubular, unsupported sheet, or thin-layer supported sheet membranes. Several companies have manufactured thin PDMS supported membranes over the years.

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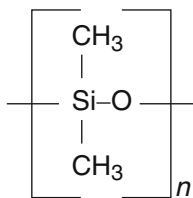
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Poly(dimethylsiloxane) [PDMS] is often referred to as the “silicone rubber.” In the PDMS structure

Polydimethylsiloxane Membrane, Fig. 1 The chemical structure of the poly(dimethylsiloxane)-repeating unit



Polydimethylsiloxane Membrane, Table 1 Permeability and selectivity data of different gasses and vapors in PDMS RTV 615 (General Electric), measured at 40 °C (Blume et al. 1991). 1 barrer = $1 \cdot 10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot (\text{cm} \cdot \text{sec} \cdot \text{cmHg})^{-1}$

Gas/vapor	Permeability, barrer	Ideal selectivity over N ₂
N ₂	280	—
O ₂	600	~2
CO ₂	3200	~12
H ₂ O	23,000	~80
C ₂ H ₅ OH	45,000	~160
Chloroform	283,000	~1000
Toluene	1,460,000	~5200

(Fig. 1), the (–Si–O–Si–) backbone is highly flexible compared to many other rubbery polymers, and interactions between the individual PDMS segments are relatively weak. Consequently, PDMS has one of the lowest glass-transition temperatures for polymers of –127 °C, which allows long-range segmental motions even at very low temperatures resulting in one of the lowest diffusivity selectivity for permeation.

PDMS can be used to fabricate hollow fiber; tubular, unsupported sheet; or thin layer-supported sheet membranes. PDMS also has very interesting properties as a membrane material, and these properties have been utilized for a long time in membrane technology practice. Silicone rubber is extremely permeable and has adequate vapor/inert gas selectivity for the most applications (Table 1). The values may vary for different types of prepolymer solution and cross-linking agent and the chosen ratio. Mixed gas permeabilities deviate from the pure gas permeabilities.

The differences in permeability of vapor molecules through PDMS are mostly governed by their solubility coefficients rather than their

diffusivity coefficients. Penetrant solubility in rubbery polymers frequently increases with pressure, particularly for organic vapor penetrants, leading to a corresponding increase in permeability. As a result of the interaction between these factors, the permeability coefficients of low-sorbing penetrants, such as H₂, which do not plasticize PDMS and have essentially pressure-independent solubility coefficients, decrease very slightly with increasing penetrant pressure. In contrast, the permeability coefficients of more soluble penetrants, such as C₃H₈, which induce significant plasticization and have solubility coefficients that also increase with pressure, increase with increasing pressure (Merkel et al. 2000).

PDMS is the current benchmark hydrophobic pervaporation membrane material used, for instance, in the removal of VOC components from aqueous streams. Several companies have manufactured thin PDMS-supported membranes over the years. At present, Membrane Technology and Research (MTR), Inc., of Menlo Park, CA, is the leading supplier, manufacturing spiral wound modules out of their supported silicone rubber membranes. Ethanol–water separation factor for PDMS membranes ranges from 4.4 to 10. Butanol–water separation factors for PDMS also cover a fairly broad range, from 40 to 60. PDMS will, at least for the near term, continue to be the dominant organic membrane material for the recovery of alcohols from water (Vane 2005).

PDMS coatings are applied on a large scale in solvent-resistant nanofiltration to separate low molecular weight components from solvents such as toluene. PDMS coatings are applied to plug defects in gas separation membranes. In all these examples, the high permeability of PDMS is exploited (de Jong et al. 2006).

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Polyelectrolyte Membrane for OSN

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Polymeric charged nanofiltration (NF) membranes have received a growing interest for water desalination and purification. Selective properties of charged NF membranes can be based upon not only the “sieving effect” but also the “charge effect.” Thus, the surface charge density of the membranes and the structure of the functional groups in the selective layer are imperative factors to determine their performance.

The range of NF applications has recently been broadened to organic feeds in organic solvent nanofiltration (OSN), also known as solvent-resistant NF (SRNF). A more widespread use of OSN requires solvent-resistant membranes that preserve their separation characteristics under more aggressive conditions of aprotic or strongly swelling solvents and elevated temperatures (Vandezande et al. 2008).

Alternate layer-by-layer (LbL) deposition of polyelectrolytes (PEs) of opposite charges has emerged as a versatile and inexpensive method to prepare thin films in the nanometer range for different applications (Decher 1997). A number of parameters, such as PE type and molecular weight of the PE, ionic strength, and pH of the

PE solutions, can influence the structure of the PE multilayer (PEM) films deposited by the LbL method. Films prepared via this method are in particular attractive materials with controlled thickness and surface properties for OSN (Li et al. 2008; Ahmadiannamini et al. 2012a).

PEs can be regarded as strong or weak depending upon degree of ionization of charged species. It is identified as strong when the dissolved PE dissociates completely and as weak when it is partially ionized. Charge density of weak PEMs can be affected by more factors than with strong ones, such as salt concentration and pH. This offers more possibilities to control membrane morphology and performance. A higher charge density is expected to lead to thinner deposited layers. Indeed, the self-repulsion of the chains is increased, and such polymer chains thus possess a larger cross-sectional area in solution, thus covering a larger surface upon adsorption on the substrate (Schönhoff 2003).

Both weak and strong PEs have been used for the buildup of PEM membranes. Comparison of their NF and OSN performances reveals that contrary to the applications in aqueous NF, PEM membranes constructed from weak PEs have retentions comparable to those of membranes prepared from strong PEs (Tables 1 and 2) (Ahmadiannamini et al. 2012a).

Another important parameter which can influence properties of PEMs is the charge density (ionic cross-linking) of the multilayer which is defined as the number of ion pairs per number of carbon atoms in the repeat unit (Krasemann and Tieke 2000). PEMs with higher ionic cross-link densities shrink less drastically in organic solvents and show higher permeances.

A very complex interplay of different contributions caused by mutual PE-solvent-solute-membrane interactions has to be taken into

Polyelectrolyte Membrane for OSN, Table 1 NF performance of PEM membranes in aqueous applications

Membrane	Permeance ($\text{l.m}^{-2}.\text{bar}^{-1}.\text{h}^{-1}$)	Retention (%)	
		Cl^-	SO_4^{2-}
(PAA pH 4.5/PDADMAC pH 4.5) _{4,5}	12.15 ± 4.34	-4.4 ± 4.3	24 ± 14
(PSS/PDADMAC) _{4,5}	20.83 ± 0.86	-15.5 ± 1.4	92.3 ± 0.9
(PDADMAC/SPEEK) ₅	15.6 ± 1.04	15.9 ± 4	93.9 ± 1

Polyelectrolyte Membrane for OSN, Table 2 OSN performance of PEM membranes in solvent applications (RB in IPA)

Membrane	Permeance ($\text{l.m}^{-2}.\text{bar}^{-1}.\text{h}^{-1}$)	RB retention (%)
(PAA pH 4/PDADMAC pH 7) ₅	0.03	97.0 ± 2.1
(PDADMAC/SPEEK) ₅	0.08	98.2

Polyelectrolyte Membrane for OSN, Table 3 Comparison of performance between PEM membranes and other OSN membranes

Membrane	RB/IPA		RB/DMF	
	Permeance ($\text{l/m}^2.\text{h}.\text{bar}$)	Retention (%)	Permeance ($\text{l/m}^2.\text{h}.\text{bar}$)	Retention (%)
Multilayered PEC	0.12–1.57	>99	0.06–0.2	94–98
Polypyrrole	1.42	98	0.03	90
PDMS	0.086	91	n.m.	n.m.
Poly(sulfone)	0.14	77.5	n.m.	n.m.
Poly(sulfone)/SPEEK	0.47	95.6	n.m.	n.m.
Starmem™ 120	0.49	100	—	—
Starmem™ 228	0.087	99.6	—	—
Starmem™ 240	0.29	97.9	—	—
MPF-50	0.72	96	—	—

n.m. not measured

— unstable in the solvent

account. PEM membranes are stable in a wide variety of organic solvents, and their performance is better than that of the different commercial membranes (Table 3), as very high retentions are combined with superior fluxes (Ahmadiannamini et al. 2012b).

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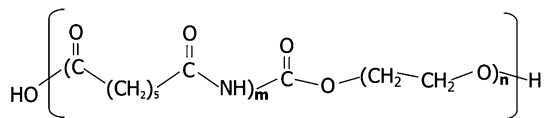
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Polyether Block Amide (PEBAX)

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Polyether block amide is a multiblock copolymer with two types of segments, rigid polyamide (PA) and flexible polyether known under the trade name Pebax® (<http://www.pebax.com/sites/pebax/en/home.page>). It is obtained by



Polyether Block Amide (PEBAX), Fig. 1 Chemical structure of Pebax[®]

polycondensation reaction (Fakirov 2005) of a carboxylic acid polyamide (PA6, P11, P12) with an alcohol-terminated polyether either polytetramethylene glycol (PTMG) or polyethylene glycol (PEG) with general chemical structure (Fig. 1):

Pebax[®] consists of a linear chain of polyamide and polyether segment (block) in an orderly pattern and belongs to the group of thermoplastic elastomers (Holden et al. 1996). The combination of the rigid PA segment and the flexible polyether segment yields a block copolymer that exhibits a microphase-separated morphology (Bates 1991) due to the polarity differences between them: a crystalline PA and an amorphous polyether phase. The crystalline phase allows the copolymer to behave as a thermoplastic and the amorphous phase imparts elastomer characteristics. The PA block melts in the range 130–200 °C (Rulkens et al. 2012); the exact value depends on average molecular weight and content of the PA in the copolymer. Polyether block crystallizes at low temperatures, the value of which lies between –30 °C and 20 °C mostly depending on its molecular weight of the sequences (Bailey and Koleske 1976). The glass-transition temperature (*T_g*) is about –50 °C due to the flexible segment (Patel and Spontak 2004). Through a proper combination of the polyamide and the polyether blocks, a wide range of Pebax[®] grades with a variety of end-use characteristics can be designed (Pebax[®] Technical Data Sheets). In general, these polymers possess a broad range of flexibility without the use of additives while maintaining high strength and toughness. Because of the thermoplastic qualities, it can be easily processed, extruded, and shaped at elevated temperatures, and upon cooling, its elasticity will allow it to return to its original length or shape after being stretched, compressed, or deformed. Depending on the nature and the relative content of both

segments, certain grades of Pebax[®] copolymers have great film-forming ability; thus, they attracted greater attention as a promising membrane material (Blume et al. 1990). The material offers strong resistance to a range of chemicals, and it is not affected by exposure to saline or sulfuric acid (Carson et al. 2010). It can be sterilized by a variety of methods including gamma radiation and steam autoclave. Pebax[®] is considered as a high performer among its thermoplastic elastomer peers because it is lightweight and because it offers a wider range of flexibility and hardness, a higher energy return, a greater resistance to fatigue, and better dimensional stability under physical and thermal stress (McKeen et al. 2010).

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Polyetherimide Membrane

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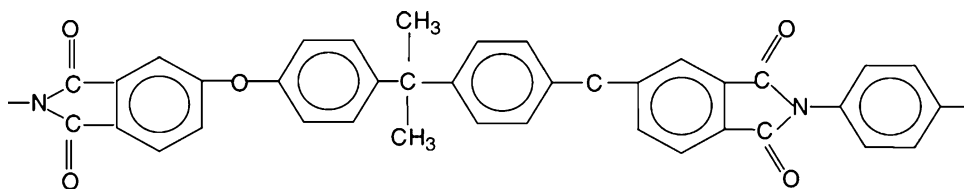
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Polyetherimide (PEI hereafter) is one of the derivatives of a broad class of materials known as polyimides. PEIs are thermoplastics having excellent chemical and mechanical stability with high glass transition temperature and find its usage in numerous applications. Polyimides are polymers containing imide group sandwiched between two aromatic rings as shown in the Fig. 1. In order words, in polyimides, a nitrogen atom is shared between two carbonyl functions (Seifert et al. 2002). PEIs can be prepared by two different schemes, one of which involves nucleophilic substitution reaction and the other scheme consists of condensation reaction between diamines and dianhydrides. The latter method is more commonly employed than the former (Sedigh et al. 1999).

Further, PEI, a derivative of polyimide, is obtained by inserting ether groups within the polyimide backbone. The presences of ethereal linkages provide good processability, while aromatic groups attribute high performance characteristics. In recent years, there has been a number of reports projecting PEI membranes as a suitable material for biotechnological and biomedical applications since the requirements for biomedical applications are rather too stringent to be satisfied by other polymeric membranes. For

instance, development of biohybrid organ such as the liver support system would require a membrane material to have biocompatibility with blood and tissue cells at the same time (Seifert et al. 2002). A major advantage of the inherent structure of PEI membranes is the presence of polarized carbonyl groups that can be easily functionalized using different ligands and groups as per the requirement. Surface functionalization of PEI could produce membranes that are compatible with blood on one side and with tissue cells on the other side. Recent reports have indicated that PEI possesses excellent mechanical strength and thermal stability and high glass transition temperature. These properties together with its ability to allow attachment and growth of cells and almost insignificant cytotoxicity to cells make it the most promising biomaterial for biotechnological and biomedical applications (Seifert et al. 2002). Further, the PEI polymers can be used for preparing highly asymmetric membranes for selective separation of pair of gases, such as binary mixtures of H₂ and CH₄, CO₂ and CH₄, and CO₂ and N₂ and ternary of CO₂/H₂/CH₄ etc. (Shen et al. 2004; Park and Lee 1995; Ahmad et al. 2010; Sedigh et al. 1999). These are difficult separations, which can only be achieved by these membrane processes, and are widely used in industry these days. Moreover, PEI membranes can also be used in ultrafiltration and microfiltration and in vapor permeation of water/1-propanol, but its use is limited by the low hydrophilic nature of PEI membranes (Shen et al. 2004; Li et al. 2008).

The excellent properties of PEIs have been utilized by blending it with other well-known polymers thereby widening the scope of its utilization and application. Reports have indicated that PEI could be used to reduce the swelling as



Polyetherimide Membrane, Fig. 1 General structure of a polyetherimide (PEI)

well as improve mechanical stability of sulfonated (ether ether) ketone (SPEEK) membranes when blended in small proportion with SPEEKs (Bowen et al. 2004). Carbon molecular sieve (CMS) membranes have been extensively used for removal of CO₂ from natural gas as they have pores of relatively uniform dimension which aids in discrimination of molecules of very similar dimensions (Sedigh et al. 1999). CMS membranes are prepared by carbonization of PEI precursors and find extensive application in solving crucial environmental problems such as removal of sulfur from gasoline by pervaporation process (Changewi et al. 2009). Applications of PEIs abound in the biomedical domain as evident from a recent report where PEIs functionalized with groups such as hydroxyl (-OH), amines (-NH_x), carboxylic acids (-COOH), and sulfate (-SO₄) have been reported to be successful in preventing thrombosis, a major complication that results from a foreign surface that comes in contact with blood. Of these, PEIs functionalized with carboxylic acid have been reported to possess the best blood-contacting properties (Tzoneva et al. 2008).

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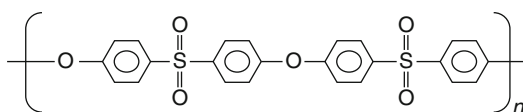
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Polyethersulfone (PES)

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Polyethersulfone (also called 4,4'-sulfonyldiphenol polymer, poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene), or poly(oxy-p-phenylsulfonyl-p-phenylene), abbreviated as PES) is an amorphous, transparent, and pale amber high-performance thermoplastic consisting of repeating phenyl groups linked by thermally stable ether and sulfonic (-SO₂-) groups. Its structure, as shown in Fig. 1, is similar to that of polyetheretherketone, but a sulfonic group replaces the right-hand -O-phenyl-CO- section. PES is the most temperature-resistant transparent commercially available thermoplastic. It has relatively high water absorption, and, in common with many other plastics, drying is essential before, e.g., thermoforming. It has poor fatigue characteristics and is prone to environmental stress cracking but has good long-term thermal aging resistance and reasonable radiation resistance. It belongs to high Tg polymers. Generally, PES possesses high



Polyethersulfone (PES), Fig. 1 Chemical structure of polyethersulfone

mechanical intensities, thermal stabilities, and chemical resistances. In addition, it has low creep properties, flame retardancies, excellent insulation properties, high dielectric strengths, and the lowest smoke-emission ratings among plastics.

PES was first manufactured by ICI Company (UK) in 1972. Nowadays, the main trade names and manufacturers of PES are Victrex TM (ICI company, UK), Ultrason TM (BASF company, Germany), and AstyleTM (3M company, USA). Both neat and reinforced grades are available in granule form for extrusion and molding. Unreinforced grades are used in high-temperature electrical applications, bakery-oven windows, and medical components. Reinforced grades are used for radomes, structural aircraft and aerospace components, and corrosion-resisting applications in packaging and chemical-plant hardware. PES is also widely used in aviation, microelectronics, automobile, membrane separation, etc. In membrane separation fields, PES has been prepared to ultrafiltration, reverse osmosis, and nanofiltration membranes. Filter cartridges made from PES membranes offer extremely high flow rates at very low differential pressures when compared with nylon or polypropylene media. Additionally filter cartridges made from PES can be sterilized within line steam or in the autoclave without loss of integrity up to 50 times.

For functional application, PES is often used as a copolymer. Sulfonated polyethersulfones (SPES) are synthesized as a promising material candidate among many other aromatic hydrocarbon-based polymers for highly durable, proton exchange membrane in proton exchange membrane fuel cell applications (Hickner et al. 2004). The biggest challenge for SPES application in fuel cells is improving its chemical durability (Borup et al. 2007). Under oxidative environment, SPES can undergo sulfonic group detachment and main chain scission. However the latter is more dominant; midpoint scission and unzip mechanism have been proposed as the degradation mechanisms depending on the strength of the polymer backbone (Lawrence and Yamaguchi 2008).

PES is also widely used as biomaterials due to its thermal stability, mechanical strength, and chemical inertness. Heparin-like poly(ethersulfone) (HLPES), with ionic groups of

$-\text{SO}_3\text{Na}$ and $-\text{COONa}$ on its macromolecule, is also synthesized by a combination of polycondensation and post-carboxylation methods. HLPES show good blood compatibility and good cytocompatibility (Wang et al. 2013).

PES allows easy manufacturing of membranes, with reproducible properties and controllable size of pores down to 40 nm. Such membranes can be used in applications like hemodialysis, wastewater recovery, food and beverage processing, and gas separation (Zhao et al. 2013).

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Polyethersulfone Membrane

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Polyethersulfone (PES) membrane is one of the most important polymeric membrane and is widely used in separation fields. PES membranes show outstanding oxidative, thermal, and

hydrolytic stability as well as good mechanical property. The membranes always show asymmetric structure and are prepared by a phase inversion method. The membrane structure is influenced by the composition such as concentration, solvent and additives, and temperature of PES solution, the non-solvent or the mixture of non-solvents, and the coagulation bath or the environment, and so on (Barth et al. 2000).

Polyethersulfone is considered one of the most important polymeric materials for use in membrane applications. With transparent and amorphous properties and a high T_g (225 °C), this polymer has high mechanical, thermal, and chemical resistances, making it ideal for use in preparing asymmetric membranes with different pore sizes and surfaces. Compared with multiple membrane materials, PES has low hydrophilic properties. Significant research has been reported on efforts to change the surface properties of the PES hydrophobic membranes (Van der Bruggen 2009). PES membrane is stable in water and is an inert membrane and acts as only as a barrier in separation process, thus not fitted to the advanced separation fields, such as intelligent separation.

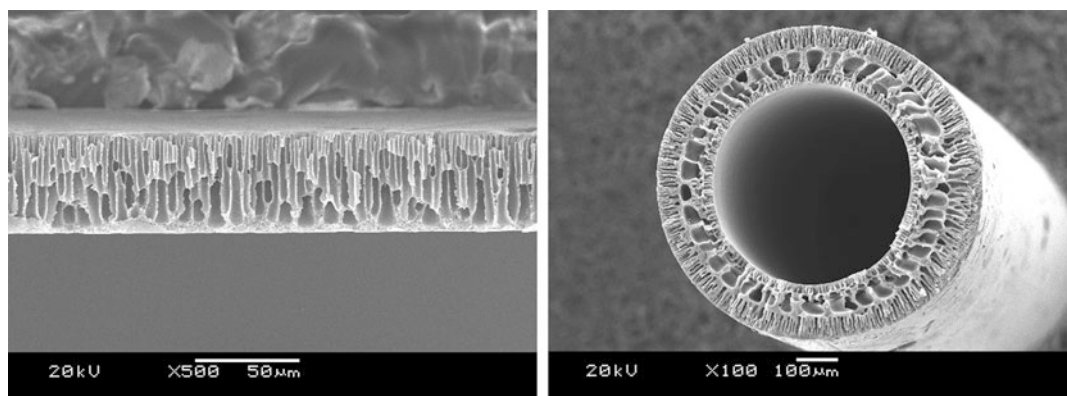
There are two main membrane shapes, flat-sheet and hollow fiber membranes. Due to the different shapes, the preparation process is different. For flat-sheet PES membrane, phase inversion technique is usually used. The polymer solution was cast on a support material (glass, polymer, metal, nonwovens), and after immersing into non-solvent

(usually water), flat-sheet PES membrane will be obtained. However, for hollow fiber PES membranes, a professional apparatus containing at least a spinneret and a take-up unit is needed. PES hollow fibers are prepared by a dry-wet-spinning technique (wet-spinning technique is seldom used) based on phase inversion (Khayet and Garca-Payo 2009). The typical field emission scanning electron micrographs of flat-sheet and hollow fiber PES membrane is shown in Fig. 1.

PES membranes are widely used in water treatment, protein and enzyme filtration sterilization, biological fluid filtration sterilization, tissue culture media sterilization, and pharmaceutical sterilizing filtration. PES membrane filters are composed of PES and manufactured within a tight specification range to ensure a uniform pore structure for low binding applications where reliable fast flow rates and high throughputs are required. PES filters are hydrophilic and can withstand high temperatures 135 °C (275 °F) without membrane degradation as required for autoclaving applications. It is also widely employed in biomedical fields such as artificial organs and medical devices used for blood purification (hemodialysis, hemodiafiltration, hemofiltration, plasmapheresis and plasma collection) (Ran et al. 2014).

Though PES membranes have been widely used, they have disadvantages. The main disadvantage of the membrane is related to its relatively hydrophobic character. So the current trend is to develop new membrane materials and structures specifically in

P



Polyethersulfone Membrane, Fig. 1 Field emission scanning electron micrographs of flat-sheet (*left*) and hollow fibers (*right*) PES membrane

view of reducing fouling effects, biocompatibility, and other functions. For the modification of PES membranes, there are three approaches: bulk modification of PES material, and then to prepare modified membrane; surface modification of prepared PES membrane; and blending, which can also be regarded as a surface modification. The modification procedures allow finding a compromise between hydrophobicity and hydrophilicity, localize the hydrophilic material specifically in the membrane pores, where they have a positive effect on flux and fouling reduction, and endow functions of membranes such as good blood compatibility and stimuli-responsivity (Zhao et al. 2013).

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Polyethylene Membrane

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Polyethylene (PE) is a polymer obtained by polymerization of ethylene. Polyethylene is produced

in three different grades depending on the polymerization processes: low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE). Polymerization of ethylene is carried out in the presence of Ziegler-Natta catalyst, and the reaction mechanism involves three steps, namely, initiation, propagation, and termination. The properties of the polymer depend on the operating temperature, pressure, and the reaction time. Temperature control is critical in the polymerization process due to the exothermic nature of the reaction. PE-based membranes are highly versatile and have been investigated for quite some time for numerous applications such as fuel cell research, biotechnology, and biomedical applications including applications involving environment monitoring (Amada et al. 1994; Matsuyama et al. 2003; Sherazi et al. 2013).

Recent reports have shown that surface-functionalized porous PE membranes have large protein adsorption capacity and are preferred over inorganic materials for binding large quantity of biomolecules. In particular chemically modified sintered porous PE-based membranes have been found to have a number of advantages. These membranes are cost-effective; the textural parameters such as pore size, pore volume, pore size distribution, and surface area can be easily tuned and consequently find applications in separation and purification of proteins including peptide synthesis (Greene et al. 2005). Another phenomenal application of nanoporous PE membrane is in the development of glucose sensors that would detect, quantify, separate, and control transport of glucose. Such devices are absolutely essential for people suffering from diabetes (Uehara et al. 2011). LLDPE membranes are used in packaging industry because of their excellent mechanical and gas transport properties. It has been reported that the gas permeability (P) through these membranes increases according to the following order $P(\text{CO}_2) > P(\text{He}) > P(\text{O}_2) > P(\text{N}_2)$ in the temperature range 298 to 348K, and the diffusion coefficient for these gases follows the following order $D(\text{He}) > D(\text{O}_2) \geq D(\text{CO}_2) \geq D(\text{N}_2)$. The disagreement in the trend for permeability and diffusion coefficients highlights that mass transport through the

membrane is dependent on the solution process (Villaluenga and Seoane 2001).

High cost of the proton exchange membranes coupled with the use of precious metals (such as platinum and ruthenium) as catalyst has largely affected the commercialization of polymer electrolyte membrane fuel cells, and consequently the focus has shifted toward development of anion exchange membranes (AEMs) for anion exchange membrane fuel cells (AEMFCs). AEMFCs are low cost and use non-noble metal catalyst as cathode material (Sherazi et al. 2013). Recent reports have indicated the use of poly(vinylbenzyl chloride) grafted on ultrahigh molecular weight polyethylene (UHMWPE) powder by irradiating with gamma Co radiation. These polyelectrolyte membranes have been used in AEMFCs. Ultrahigh molecular weight polyethylene powder is highly stable in alkaline medium, shows tendency toward cross-linking when irradiated with gamma radiations, and is a low-cost material. Surface-modified UHMWPE membranes have been used as biocompatible materials for use in many biomedical applications. Surface modification of UHMWPE is done using underwater plasma polymerization technique since olefin polymers do not have any functional groups which make it relatively easier to introduce polar groups by plasma processes thereby attributing biocompatibility (Joshi et al. 2013). Polyethylene membranes have also been used in environmental monitoring applications especially the organochlorine pesticides such as lindane, aldrin, and dieldrin. It has been reported that polyethylene membranes have 24–84 times higher chemical uptake capacity as compared to the cellulose membrane. However, it is also known that the solvent retention time is low for polyethylene membranes and the rate of diffusion of chemicals is dependent not only on the molecular mass of the chemical species but also on the solubility in lipids [8].

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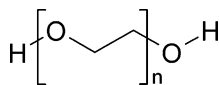
Polyethylene Oxide

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Polyethylene oxide (PEO) is a polymer prepared by polymerization reaction (polycondensation) of ethylene oxide and water catalyzed by acidic or basic catalysts (Hideshi 1995). It has two chemically synonymous names: poly(ethylene glycol) (PEG) and poly(oxyethylene) (POE) (Buchmeister 2003). PEG has tended to refer to oligomers and polymers with a molecular weight below 20,000 g/mol, PEO to polymers with a molecular weight above 20,000 g/mol, and POE to a polymer of any molecular weight with the general formula $H(OCH_2CH_2)_nOH$ (Fig. 1), commercially available over a wide range of molecular weights (<http://www.sigmaaldrich.com/materials-science/material-science-products.html>), where n is the average number of repeating oxyethylene

Polyethylene Oxide,
Fig. 1 Chemical structure
 of polyethylene oxide



groups (OCH_2CH_2) typically from 2 to few 100. The low molecular weight members from $n = 2$ to $n = 4$ are diethylene glycol, triethylene glycol, and tetraethylene glycol, respectively, which are produced as pure compounds (DOW). Increasing the number of repeating oxyethylene groups leads to products with different oligomer sizes in a broadly or narrowly defined molecular weight. For example, PEG 300 typically denotes a compound that includes a mixture of oligomers having an average molecular weight of 300 g/mol. Low molecular weight ($<1,000$ g/mol) PEGs are viscous and colorless liquids with freezing point from -10°C (diethylene glycol), while higher molecular weight PEGs (PEOs) are waxy, white solids with melting points proportional to their molecular weights up to limit of about 67°C (Bailey and Koleske 1976). These polymers are amphiphilic and soluble in water as well as in many organic solvents (e.g., methylene chloride, ethanol, toluene, acetone, and chloroform) including aromatic hydrocarbons (not aliphatic) (Zhao et al. 1998). Although PEG and PEO with different molecular weights have different physical properties (e.g., viscosity, melting point) due to chain-length effects, their chemical properties are nearly identical. Hence, they have multiple applications in different fields. They provide binding, thickening, lubricity, water retention, and film formation benefits to deliver excellent performance, such as in mining, paper, and cleaning products. Due to their nontoxic and nonirritant properties, they are broadly used as well in pharmacy, medicine, and cosmetics (Working et al. 1997; Andersen 1999). They are also thermoplastic materials that are readily calendared, extruded, injection molded, and cast, to provide even greater formulation and processing flexibility. The different forms of PEG are also available (Lapientis 2009; Fruijtier-Pöllöth 2005; Zalipsky 1995) depending on the used initiator during the polymerization process, the most common is a monofunctional methyl ether PEG (methoxypoly(ethylene glycol)), abbreviated as MPEG. PEGs are also available with different

microstructure. Branched PEGs have three to ten PEG chains emanating from a main chain; star PEGs have 10–100 PEG chains emanating from a central core group, and Comb PEGs have multiple PEG chains normally grafted to a polymer backbone.

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Polymer Electrolyte Membrane Fuel Cell (PEMFC)

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Fuel cells (FCs) are electrochemical devices for the direct conversion of chemical energy into electrical energy.

Polymer Electrolyte Membrane Fuel Cell (PEMFC), Table 1 Reactions occurring in hydrogen and direct methanol polymer electrolyte membrane fuel cell (PEMFC)

	H ₂ -PEMFC	Methanol-PEMFC
Anode	$\text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^-$	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$
Cathode	$\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{3}{2} \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$
Overall reaction	$\frac{1}{2} \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$	$\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

Unlike the classical battery, FCs do not store the energy within the chemicals internally, but they use a continuous supply of the fuel from an external storage tank. Moreover, while the electrodes in a battery react and change as a battery is charged or discharged, in a fuel cell the electrodes are catalytic.

Because FCs do not include the conversion of thermal to mechanical energy, they are not subject to the Carnot efficiency limit typical of a heat engine (e.g., steam and gas turbine) and are characterized by a high energy efficiency (Song 2002).

The primary components of a FC are: the anode, the cathode, and the ion conducting electrolyte. In a FC, the selective transport of ions through an electrolyte occurs in combination with a redox reaction.

In a Polymer Electrolyte Membrane Fuel Cell (PEMFC), the electrolyte is a polymer electrolyte membrane (PEM) which allows the transport of the protons from the anode, where they are produced in the oxidation of a fuel (usually H₂ or methanol), to the cathode, where the protons react with O₂ to produce water (Table 1).

The PEM is a cation exchange membrane and the flow of ionic charges (ideally only cations) through the membrane is balanced by the flow of electronic charge through the external circuit producing an electrical power. The only secondary products in the overall reaction are: water, heat (eventually recoverable), and CO₂, if the fuel contains carbon (e.g., methanol as fuel in direct methanol PEMFC).

The reaction at the anode is exothermic; however, it requires to overcome an activation energy barrier. Three strategies are used in FCs technology in order to improve the kinetic reaction: raising the temperature, increasing the surface electrode area, and using catalysts (usually Pt or Pt alloys).

The ion-exchange membrane is pressed with a porous electrode layer on each side and the catalyst is present at the interfaces membrane/electrode forming the so-called membrane electrode assembly (MEA).

A single PEMFC typically gives a voltage from 0.6 to 0.7 V, as a consequence, to produce a useful voltage, many cells are connected in series. Such a design is called fuel cell stack. Bipolar plates, generally made of graphite, interconnect the cathode of one cell with the anode of the next cell, serving in parallel the following functions: conducting electricity, feeding oxygen to the cathode and fuel to the anode, and channeling away wastewater and heat from the reaction sites.

Currently, the most commonly used PEMs for applications in PEMFCs are made of perfluoro-sulfonic acid polymers, such as Nafion membranes.

In the last decades, the development of new PEMs with improved properties for long-term fuel cells operations has received relevant attention. Not only perfluoropolymers but also partially fluorinated and nonfluorinated hydrocarbon, nonfluorinated aromatic, mixed matrix, and acid–base blend membranes, have been investigated. Various reviews are available which give an overview of the progress made in the development of proton-conducting polymer materials for PEMFCs (Roziere and Jones 2003; Hickner et al. 2004; Smitha et al. 2005; Tripathi and Shahi 2011; Thiam et al. 2011; Drioli and Fontananova 2012).

The properties required to the PEMs are: high proton conductivity; no electronic conductivity; low permeability to the reagent species; appropriate chemical, thermal, and mechanical stability; and acceptable costs.

The low operating temperatures (50–130 °C) and the high power density (400–1000 W/Kg) of the PEMFCs make them ideal for automotive applications, distributed power generation, and portable electronic devices (Larmine and Andrews 2000).

Although PEMFCs have recently passed the demonstration phases and have reached a partial commercialization stage (Wee 2007), there are still many issues to be addressed before large scale diffusion, including the high cost and limited durability of PEMs, the appropriate fuel production and storage.

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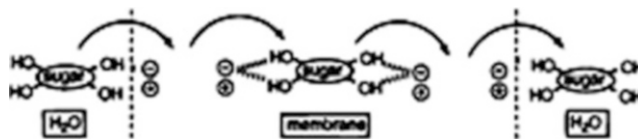
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- (PPMs), have been used for transport of solutes as an alternative to supported liquid membranes (SLMs) (Nghiem et al. 2006; Fontas et al. 2007). These membranes have also been used for metal ion uptake and sensing in ion-selective electrodes (where the ion-selective ligand can be an ionophore, an ion exchanger, or a mixture of both) and sensors (Moody et al. 1970; Scindia et al. 2002). The PIMs are known to have better stability as compared to the SLMs though the flux has been generally lower than that observed with SLMs (Paugam and Buffle 1998). However, there are some reports in which higher transport rates were observed with PIMs as compared to analogous SLMs (Kim et al. 2001). PIMs are usually made from a base polymer (such as CTA, PVC, PVDF, etc.), a carrier extractant, and a plasticizer. CTA (cellulose triacetate) and PVC (polyvinyl chloride) are some of the most widely used base polymers. While CTA works in lower acidity range, it undergoes hydrolysis at higher acidities where PVC-based PIMs have often been used. The CTA-type PIMs can have better acid/alkali resistance by increasing the chain length of the substituent though a concomitant decrease in flux may be seen when the membranes were made more hydrophobic (Gardner et al. 2004).

Organic compounds like TBP (tri-*n*-butyl phosphate) and TEHP (tri-2-ethylhexylphosphate) work both as the carrier and plasticizer and have been used for the transport of various metal ions including the actinides. However, they also suffer from the disadvantages of acid cotransport and poor decontamination from other metal ions. The PIMs, therefore, are generally made from benign plasticizers like NPOE (2-nitrophenyloctyl ether). The carrier extractant has the role of complexing with the substrate and its subsequent transport across the membrane, either by diffusional mass transfer or by a fixed-site jumping mechanism (see Scheme 1) where a threshold carrier concentration is needed (Riggs and Smith 1997). Cussler et al. have suggested a “chained carrier” model (Cussler et al. 1989) based on a percolation threshold. A model based on carrier molecule organization based on coalescence of liquid carrier-plasticizer micro-domains for the facilitated transport of the metal ions is presented in

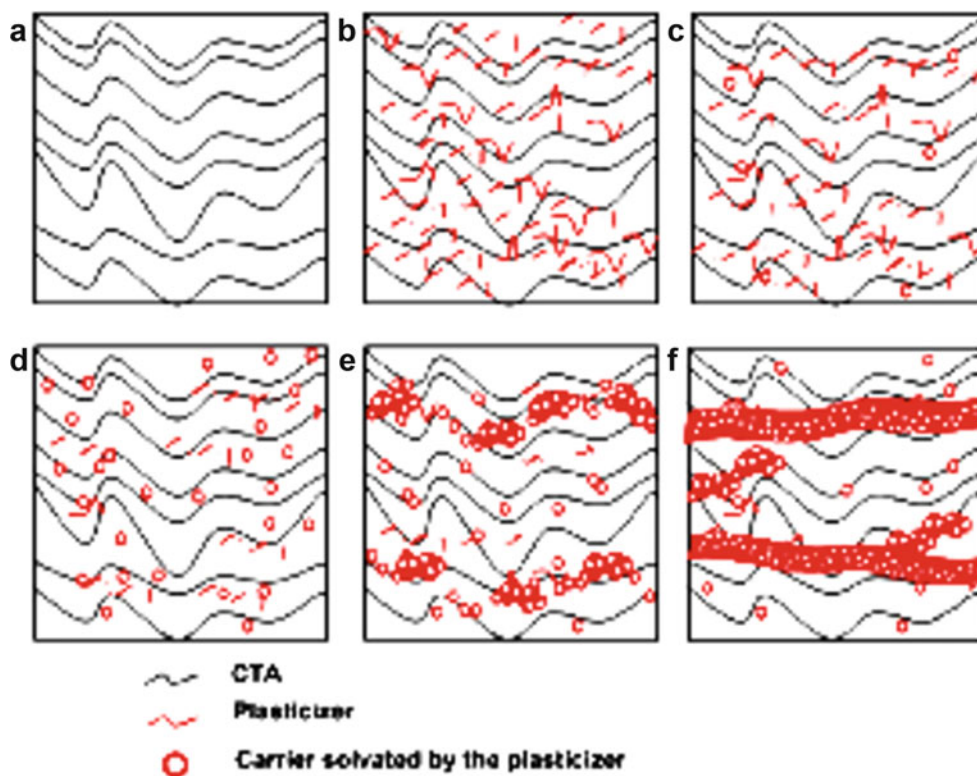
Polymer Inclusion Membranes

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Polymer inclusion membranes (PIMs), also known as plasticized polymeric membranes



Polymer Inclusion Membranes, Scheme 1 Postulated fixed-site jumping transport mechanism (Reproduced with permission from Riggs and Smith 1997)



Polymer Inclusion Membranes, Fig. 1 Organization of the PIM structure as a function of the carrier concentration: (a) only CTA; (b) CTA + plasticizer; (c–e) CTA + plasticizer + carrier (low concentration); (f): CTA + plasticizer +

carrier (high concentration leading to formation of micro-domains) (Reproduced with permission from Fontas et al. 2007)

the Fig. 1 below (Fontas et al. 2007). In many cases, the plasticizer reduces the glass transition temperature and imparts the PIM optimum physical characteristics required for the mobility of the ions or their complexed species. Also, the plasticizers make the PIMs less porous and homogeneous which facilitate mass transfer. While the base polymer imparts mechanical strength, the plasticizer makes the membranes flexible and facilitates the mass transfer by reducing

interactions between the polymeric strands and also by diffusion through a liquid phase similar to the SLM.

PIMs have been extensively used for the removal of toxic and heavy metals from wastewater which include anionic species like CrO_4^- (generally recovered using basic extractants like Alamine 336 or Aliquat 336) and cationic species like Pb^{2+} and Cd^{2+} (generally recovered using chelating extractants). Apart from the anionic

and cationic species transport, PIMs have also been used for neutral (Sakai et al. 2010) species transport. There have also been reports on PIM-based hollow fibers for possible large-scale processing (Kusumocahyo et al. 2006).

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Polymer with Intrinsic Microporosity (PIM)

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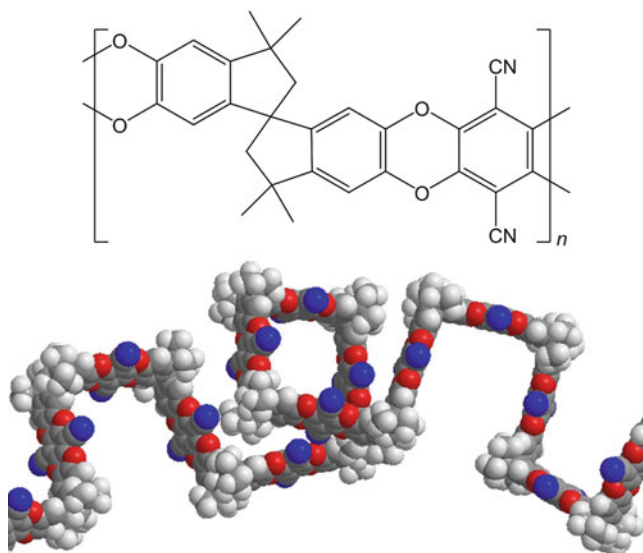
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A polymer of intrinsic microporosity (PIM) is an amorphous, glassy polymer that contains interconnected pores of width less than 2 nm, which arise directly from the shape and rigidity of the component macromolecules (McKeown and Budd 2010). This type of polymer behaves like a microporous material or molecular sieve in a low-temperature nitrogen adsorption experiment, exhibiting high uptake at very low relative pressure. It must be emphasized that in this context, the term “microporous” refers to pores with dimensions on the molecular scale. The term “intrinsic microporosity” was originally applied to polyphenylene oxide polymers that showed evidence of an interconnected system of microcavities (Illinitch et al. 1999). It was subsequently used for polymers with backbones composed of rigid sequences linked by sites of contortion that force the backbone to twist and turn (Budd et al. 2005). These polymers possess high free volume in the solid state, because the component macromolecules cannot fill space efficiently. The prime example of a soluble, membrane-forming PIM is referred to as PIM-1 (Fig. 1).

In PIM-1, there are no single bonds in the backbone about which rotation can occur, and so it cannot undergo large-scale conformational change in the way a conventional polymer can. The spiro-center (two five-membered rings with a carbon atom in common) acts as a site of contortion, putting a bend in the chain and making it difficult for chains to align and pack together. The intrinsic microporosity, coupled with the organic nature of its backbone, gives PIM-1 a high affinity for small organic molecules, which are readily adsorbed from the vapor phase or from aqueous solution. PIM-1 is soluble in solvents such as

Polymer with Intrinsic Microporosity (PIM),

Fig. 1 Molecular structure of PIM-1 and molecular model of a fragment of PIM-1 showing its contorted shape



chloroform and tetrahydrofuran and can be processed from solution to form yellow, fluorescent, thermally stable membranes or coatings. PIM-1 membranes have been investigated for a variety of liquid, gas, and vapor separations. In pervaporation, PIM-1 exhibits organophilic character, being selective for organic species rather than water (Budd et al. 2004). In organic solvent nanofiltration, it separates smaller species from larger species (Fritsch et al. 2012). In gas separation, it helps to define the 2008 upper bound of performance for gas pairs such as CO_2/CH_4 , CO_2/N_2 , and O_2/N_2 (Robeson 2008). A variety of chemical modifications have been carried out on PIM-1 in order to tailor the transport properties.

A wide range of PIMs have been prepared, including both soluble, membrane-forming polymers and insoluble network polymers (McKeown and Budd 2010). In addition to spiro-centers, units that have been used as sites of contortion include ethanoanthracene and triptycene. PIMs are often synthesized by a step-growth polymerization involving a double nucleophilic aromatic substitution reaction between a monomer bearing pairs of hydroxyls and a monomer bearing pairs of fluorines. A recent development is the use of Tröger's base formation as a novel polymerization method (Carta et al. 2013).

Any polymer that possesses sufficient interconnected free volume as to allow the ready

uptake and transport of gasses and vapors may be regarded as having "intrinsic microporosity." This includes highly permeable, glassy polymers such as poly(1-trimethylsilyl-1-propyne) (PTMSP), in which it is the bulky trimethylsilyl side group which restricts flexibility of the backbone and forces it into a twisted shape.

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Polymeric Catalytic Membranes

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A polymeric catalytic membrane is a polymeric membrane with catalytic properties. The base material used to prepare the membrane is a polymer, and a catalyst is immobilized within the membrane or on its surface, conferring catalytic activity to the system.

Moreover, some polymeric membranes can have intrinsic catalytic properties towards some reactions because of the presence of specific functional chemical groups in the polymer material. This is the case of acid polymeric membranes, like Nafion (a perfluorosulfonic acid polymer), which can work as solid acid catalysts.

Polymeric catalytic membranes are usually employed when the reaction temperatures are

low (<200 °C), such as in the field of fine chemicals or when a biocatalyst is present (Vankelecom 2002).

The use of polymeric catalytic membranes has a lot of interest in the field of membrane reactors because: a much wider choice of polymeric materials is available (Ulbricht 2006), the cost of the polymer membranes is generally lower, and the preparation protocols are more reproducible in comparison with inorganic membranes.

Polymeric membranes are generally less resistant to high temperatures and aggressive chemicals than inorganic ones; however, some polymeric materials resistant under rather harsh conditions are available like: polydimethylsiloxane (PDMS), polyvinylidene fluoride (PVDF), Hyflon (a perfluoro amorphous polymer), Nafion, and polyimides (PI) (Drioli and Fontananova 2010).

Some selected examples of polymeric catalytic membranes used in membrane reactors are listed in Table 1.

Polymeric Catalytic Membranes, Table 1 Selected examples of polymeric catalytic membranes used in membrane reactors

Catalyst and membrane type	Applications	References
Metal or bimetal nanoparticles in porous membranes: Pd in PAA ^{a,b} Au-Pd/PVP in PI ^c	Selective hydrogenation in gas ^a and liquid phase ^b Oxidation of alcohols ^c	^a Groschel et al. 2005 ^b Schmidt et al. 2005 ^c Mertens 2008
Catalyst in dense membranes: FePcY in PDMS ^d Transition metal complexes with bisphosphine ligands in PDMS ^e	Cyclohexane oxidation ^d Enantioselective hydrogenation of methyl 2-acetamidoacrylate ^e	^d Vankelecom et al. 1996 ^e Wolfson et al. 2002
Enzymes immobilized in UF membranes: Lipase from <i>Candida rugosa</i> in PA capillary membranes ^f Lipase from <i>Serratia marcescens</i> in hollow fibers hydrophilic membranes ^g	(S)-Naproxen esters hydrolysis ^f (-)-MPGM resolution by Sepracor reactor (industrial application)	^f Giorno et al. 2007 ^g Shibatani et al. 2000
Acid membranes and/or membranes functionalized with solid acid catalysts: PVA/sulfosuccinic acid ^h , Nafion ^h , supported acid catalysts mixed with a polymeric binder on PAN/PDMS ^{i,j}	Transesterification of soybean oil ^h Esterification reaction ⁱ Dimerisation of isobutene ^{i,j}	^h Guerreiro et al. 2006 ⁱ Bagnell et al. 1993 ^j Fritsch et al. 2004
Polyoxometalates immobilized in/on porous or dense membranes: Porous PVDF ^{k,l} , dense Hyflon ^m Surface functionalized PVDF ⁿ membranes	Photooxidation of alcohols in water ^k Phenol photodegradation ^{l,n} Photooxygenation of hydrocarbons ^m	^k Bonchio et al. 2003 ^l Drioli et al. 2008 ^m Carraro et al. 2006 ⁿ Fontananova et al. 2006

PAA polyacrylic acid, FePcY iron phthalocyanine in zeolite Y, PA polyamide, PVA polyvinyl alcohol, MPGM (3-(4-methoxyphenyl)glycidic acid methyl ester), PVP polyvinylpyrrolidone, PAN polyacrylonitrile, PVDF polyvinylidene fluoride

In classical heterogeneous catalysis (catalyst absorbed or linked in porous polymeric or inorganic solids), the conversion and selectivity of the catalytic process is often limited by the diffusion of the reagents to the catalytic sites and the products removal from them.

On the contrary, the convective or diffusive flux in a catalytic membrane can be easily controlled and adjusted to the reaction kinetic modulating the driving force and/or the membrane structure and/or membrane material (Westermann and Melin 2009).

Moreover, in a catalytic membrane, especially if polymeric, the catalyst entrapment in the functional microstructured environment of the membrane can have a positive influence on the transition states and reaction kinetics by electronic and weak interactions, as well as by spatial restriction and transport dynamics (Fontananova and Drioli 2010).

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Polymeric Magnetic Membranes

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Synonyms

Magnetically responsive membranes

The **polymeric magnetic membranes** are polymeric membranes with dispersed granules of a permanent magnet (ferrite, praseodymium, and neodymium) or with magnetic nanoparticles (ferroferric oxides), which are intended for separation purposes (Rybak et al. 2012). As a polymer matrix the ethyl cellulose (EC) or poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) can be used.

Polymeric membranes filled with neodymium powder have been successfully used for enrichment of air by oxygen. Membranes of various polymer matrices (EC and PPO) with different types of dispersed magnetic powder (ferrite, praseodymium, and neodymium) and granulation (20–32 μm , 32–50 μm) can be prepared by solution casting and evaporation. Magnetic membranes are made by casting of 3 % EC solution in 40:60 ethanol/toluene or 2.5 % PPO solution in TCE (trichloroethylene) with dispersed magnetic powders of appropriate amount: 0.5–2 g in external field (stable magnetic field with range of induction $0 \div 40$ mT) (Strzelewicz et al. 2007; Rybak et al. 2009a; Grzywna et al. 2010). In the next step membranes are removed from Petri dish and dried in 40 °C for at least 2 days before any further analysis. The membranes were stored in an exsiccator under the vacuum conditions ($p = 3$ mmHg).

The transport of the molecules through the magnetic membranes can be modeled by a diffusion with a position-dependent diffusion coefficient. Such a diffusion coefficient reflects the changes in the membrane composition along the permeation axis (Rybak et al. 2009b; Borys et al. 2011). Magnetic membranes are inhomogeneous, i.e., on the bottom (permeation side), there are the magnetic aggregates of the magnetic powder, while on the top (feed side), there is a layer of pure polymer.

Another group of magnetic membranes are polymer membranes containing magnetic nanoparticles, i.e., ferroferric oxide particles. The membranes can be prepared as described in Dudek et al. (2012), where ethyl cellulose and poly(2,6-dimethyl-1,4-phenylene oxide) were used as polymer matrix. The membranes were prepared by solution casting and evaporation.

For proper dispersion and homogenization of magnetic particles in the polymer solution, the mixture was sonicated using high-intensity ultrasound radiation. The average thickness of the obtained membranes was 25 μm . The membranes were examined for nitrogen and oxygen permeability. Detailed description of preparation and characterization of iron oxides–polymer composite membranes is given in Dudek et al. (2012).

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Polymeric Membrane Characterization by PALS

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Synonyms

PALS

The size of free volume elements in polymeric membrane materials can be related to the average lifetime of either free positrons or ortho-positronium (o-Ps) in the polymer measured using positron annihilation lifetime spectroscopy (PALS) (Mallon 2003; Hill et al. 1996, 2005; Pethrick 1997; Liao et al. 2011). Additionally, for some polymers, the average o-Ps intensity can be combined with the average o-Ps lifetime to determine the polymer's fractional free volume (FFV) (Mallon 2003; Hill et al. 2005; Pethrick 1997; Matteucci et al. 2006). In some polymers, however, positron-polymer interactions can disrupt the relationship between o-Ps intensity and the concentration of void space (or free volume elements) in the polymer (Liao et al. 2011; Jean et al. 2003; Xie et al. 2011; Hirata et al. 1997; Kobayashi et al. 2009).

Free volume information is useful for characterizing nonporous polymer membrane materials because the diffusion coefficients of penetrants in the polymer matrix are related to the polymer's free volume (Cohen and Turnbull 1959). Many studies have correlated transport properties (e.g., permeability and diffusivity) with free volume determined using PALS (Hill et al. 1996, 2005; Matteucci et al. 2006; Xie et al. 2011; Freeman and Yampolskii 2010; Ju et al. 2010; Rowe et al. 2009; Zhang et al. 2012; Chen et al. 2012; Tung et al. 2009; Merkel et al. 2002; Nagel et al. 2002; Alentiev et al. 1997; Yampolskii et al. 1994; Kim et al. 2005). These studies include polymers for gas separation membranes and liquid (e.g., desalination) membranes. These correlations further suggest that PALS is a valuable tool for characterizing polymer free volume. In addition to correlating with transport properties, PALS data have been shown to correlate with various thermal and mechanical properties of polymers (Mallon 2003; Pethrick 1997).

The average o-Ps lifetime in a polymer can be related to the average size of the polymer's free volume elements using the Tao-Eldrup model when the average free volume element radius is around or smaller than 10 Å (Mallon 2003; Pethrick 1997; Tao 1972; Eldrup et al. 1981). In general, as free volume elements become larger,

o-Ps lifetime increases (Hill et al. 2005; Pethrick 1997). Additionally, the average free positron lifetime may be related to the size of the polymer's free volume elements (Liao et al. 2011). The Tao-Eldrup model assumes that the polymer's average free volume element size can be represented by a sphere (Mallon 2003; Pethrick 1997; Tao 1972; Eldrup et al. 1981). With this assumption, the volume of a free volume element in the polymer can be calculated geometrically using the radius obtained from the Tao-Eldrup model (Mallon 2003).

Cross-References

- [Positron Annihilation Lifetime Spectroscopy \(PALS\)](#)
- [Positron Annihilation Spectroscopy](#)

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Polymeric-Ceramic Catalytic Membrane

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Polymer membranes and ceramic membranes are two types of membranes prepared, respectively, from organic or inorganic and metallic materials. Polymer-ceramic membranes represent a different class of membranes that combines properties of both polymer and ceramic membranes. They are often named as composite or hybrid membranes and tailored regarding the targeted application. They may consist mainly of ceramic materials modified by various kinds of polymers or polymer membranes including inorganic nanoparticles, for instance.

Catalytic membranes are developed for reactive separation processes that involve reaction and separation steps either in gas or liquid phase. Indeed, they are not only acting as filtration media but also allow the reaction to take place acting as heterogeneous catalysts.

Organic-inorganic catalytic membranes are largely applied to biodiesel production (Shi et al. 2010) for the conversion of methanol and other esterification reactions requiring a high permselectivity. A growing interest is focused on applications such as photodegradation and photocatalysis (Romanos et al. 2013) using membrane processes and coupled technologies.

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Polymers for Drug Delivery

► Biodegradable Polymer for Membranes

Polymers for Tissue Engineering

► Biodegradable Polymer for Membranes

Polyphenol Recovery from Olive Mill Wastewater by Membrane Separation

N. Othman

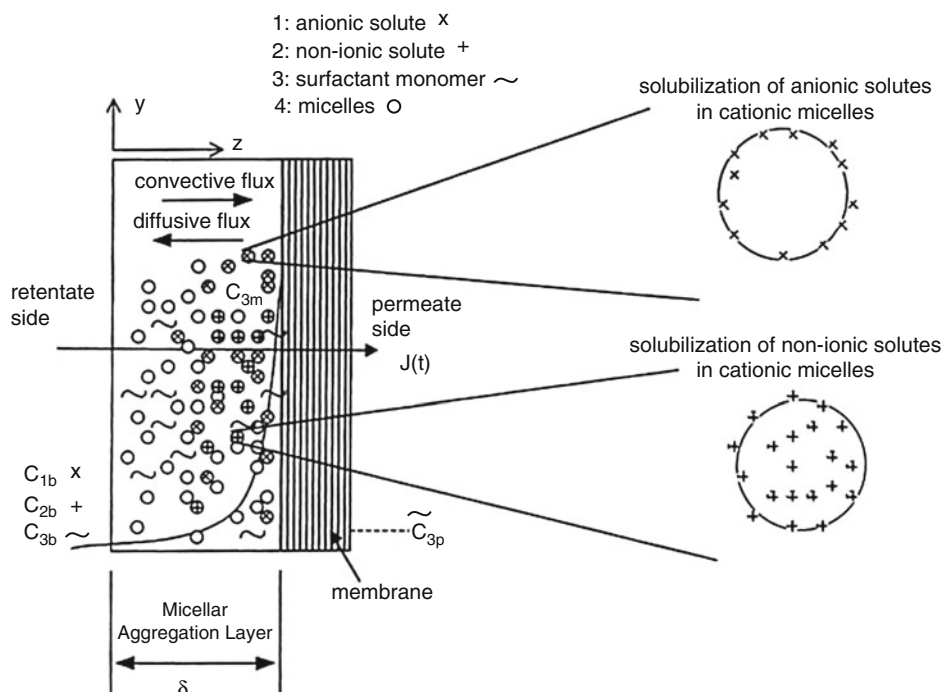
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Polyphenols are naturally occurring compounds found largely in fruits, vegetables, cereals, and beverages. In olive processing, the production of oil is about 20 %, 30 % semisolid waste, and 50 % aqueous liquor. The liquid effluent from the olive mill wastewater (OMW) was about 0.5–1.5 m³ per 1,000 kg of olive, and the wastewater was categorized as a phenolic-rich industrial effluent. The by-products from this wastewater may become important sources of high-added value compounds, such as hydroxytyrosol or other antioxidant polyphenols. Several treatment procedures including physical, chemical, biological, or combined technologies have been tested to reduce undesirable properties of OMW and recover the value-added product. One of the promising techniques is membrane separation. Membrane separation can be divided into two modes of operation such as membrane filtration and liquid membrane separation. Membrane filtration is hybrid processes that combine pressure-driven membrane processes with adsorption processes. The efficiency of this process to remove phenol with different type of membrane is about 80 % rejection (Bódalo et al. 2009).

In ultrafiltration (UF) process, the feed stream is pumped under pressure over the surface of a membrane whereby a pressure gradient is created across the membrane, and it is split into two product streams. The pressure gradient forces the solvent, and smaller species pass through the pores of the membrane while large molecules will be retained. The retained stream is also called as retentate or concentrate which is enriched with retained macromolecules but also contains some of permeable solutes, while the rest that passes through the membrane is called as permeate. Since UF deals with large molecule separation, therefore the osmotic pressure required is relatively low (Cheryan 1998).

Micellar enhanced ultrafiltration (MEUF) can be considered as a feasible membrane alternative technique which is effective and economical for removing organic matters like polyphenol from wastewater. In view of the basic principle of MEUF process, it involves the solubilization of organic solutes in the surfactant's micelle, thus increasing the size of the solutes to be separated and eventually retained by the ultrafiltration membrane. The surfactants in the aqueous or the organic solution, above critical micelle concentration (CMC), form micelles (Elworthy et al. 1968). Most of the organic solute molecules can solubilize in the micelles. Micelles being larger in size can be rejected with the solubilized organic contaminants using a relatively porous membrane under low operating pressure. The schematic diagram of the process is shown in Fig. 1.

For the studies on MEUF of phenol, ultrafiltrations were mostly carried out using flat membranes fitted in stirred or unstirred batch cells whose effective filtration areas were below 100 cm². Works by Syamal et al. (1997) showed that the retention of phenol is not good enough and usually below 70 %. From previous study, it was found that most of the researchers used micellar enhanced ultrafiltration (MEUF) to remove phenol (Tung et al. 2002; Witek et al. 2006; Purkait et al. 2005). In MEUF systems, surfactant is used and when it is added to the polluted aqueous solution above its critical micellar concentration (CMC), it will assemble and aggregate to



Polyphenol Recovery from Olive Mill Wastewater by Membrane Separation, Fig. 1 Schematic diagram of separation of anionic and non-ionic solutes by MEUF using cationic micelles (Jadhav et al. 2011)

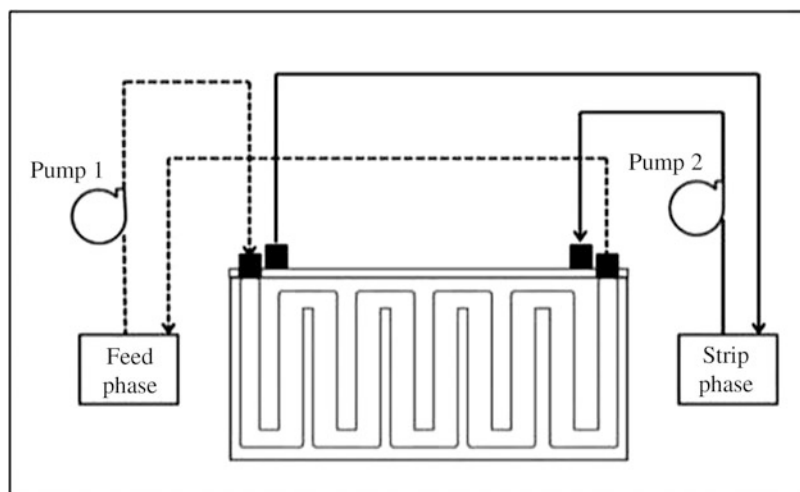
form micelle. The micelle can solubilize the organic solutes into its hydrophobic core or adsorb counter metal ions on its surface. The micelle forms large-size molecules and the separation is effective when passing through the small pore sizes of ultrafiltration membrane (Tung et al. 2002; Zeng et al. 2008). In the study of Witek et al. (2006), cationic surfactants, hexadecyltrimethylammonium bromide (CTAB) and anionic surfactant and dodecyl sulfate sodium salt (SDS), were used to investigate the rejection efficiency of phenol and chromium (Cr^{3+}). The results showed that rejection efficiency only achieved 35.2 % for SDS surfactant and 44.6 % for CTAB surfactant.

Another membrane separation technology is immobilized liquid membranes (ILMs), also called as supported liquid membranes (SLMs) where liquid is immobilized or impregnated in the pores of thin microporous solid support (Kislik 2010). The common types of SLM are flat (thin) sheet SLM and hollow fiber SLM. The greatest difference between SLM is its surface

area-to-volume ratio which is flat sheet and is too low compared to hollow fiber SLM (Kaushik 2008; Kislik 2010). In thin sheet SLM, the membrane is a porous polymer membrane whereby the pores are filled with organic liquid and carrier which is shown in Fig. 2. It is then set in between source and receiving phase which are being gently stirred. In hollow fiber SLM system, there are many thin fibers in which the pores are filled with organic phase running the length of the shell where the outer shell is a single nonporous material. The feed phase which contains the solutes desired is piped through the system from top to bottom, and the carriers in organic phase transport the solutes across to the receiving phase. The receiving phase is then forced out through the shell sides (Kaushik 2008).

Zidi et al. (2011) studied on extraction of phenol from aqueous acidic solutions using SLM with tri-*n*-octylphosphine oxide (TOPO) as carrier and kerosene as diluents. The results showed that 67 % of phenol was removed to the receiving phase,

Polyphenol Recovery from Olive Mill Wastewater by Membrane Separation,
Fig. 2 Schematic diagram of thin flat sheet-supported liquid membrane extraction



sodium hydroxide (NaOH) after 24 h of transport by using flat sheet SLM. However, Badgajar and Rastogi (2011) succeed to remove 92.5 % phenol after 20 h of transport by using flat sheet SLM impregnated with triglycerides (vegetable oils).

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Polyphenol Recovery from Wine Wastes by Membrane Operation

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Grape wastes (pomace, seeds, lees) have been recognized as an important and inexpensive source of polyphenols. Antioxidants from residual sources could be used to increase the stability of foods by preventing lipid oxidation and to protect against oxidative damage in living systems by scavenging reactive oxygen species. In addition,

significant attention has been paid for applications of antioxidants in the food, cosmetic, and pharmaceutical industries because of similar functionality requirements for the products. Traditional wine production is accompanied by generation of waste quantities of solid wastes such as seeds and pomaces. The polyphenols are mainly anthocyanins, flavonols, phenolic acids, and stilbenes (resveratrol). Studies reported antioxidant activity of the extracts, suggesting the winery by-product for production of natural antioxidants. For the recovery of polyphenols and other functional compounds, solid–liquid extraction is widely used. The industrial batch extraction of polyphenols is performed for about 20 h at 50–60 °C. Membrane separation processes are ideal for recovering and concentrating these compounds, ensuring high quality of the extracts produced. The process should be performed in order to remove the undesirable compounds present, such as proteins and sugars, which react with the phenolic compounds potentially reducing their antioxidant activity. Moreover, the removal of microorganisms and toxic substances is highly desirable. The type and the quantity of impurities in the extract may influence the filtration mechanism and efficiency of polyphenol separation. Optimization of polyphenol purification by membrane operation requires knowledge of factors influencing the filtration flux and rejection of solutes. Filtration rate is negatively influenced by the components of natural extracts (proteins, polyphenols, pectins, and polysaccharides). Cascades of membranes with different molecular cutoffs allow for the collection of the fractions of interest. Depending on the extracts, the membrane cutoff should be adapted. Membranes with MWCO below 150 kDa may be used for concentration of polyphenols from grape seed extracts. The possibility of membrane fractionation of different phenolic compounds, contained in grape seed and grape pomace extracts, was also demonstrated. The elimination of proteins is improved with coagulation–flocculation prior to membrane separation or with pH adjustment. Proteins coagulate around their isoelectric point (pH 4) and agglomerate. Proteins are retained by the ultrafiltration membrane and polyphenols are purified in

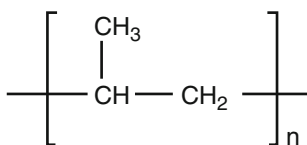
permeation. The recovery of monomeric and oligomeric compounds may be aimed for or, alternatively, the recovery of polymeric compounds. The use of nanofiltration membranes allows for obtaining fractions enriched in phenolic compounds with low molecular mass, while a different membrane selection may allow for production of a different fraction. Control of undesirable products is achieved to a much greater extent. For example, when recovering a target extract as a permeate stream in a nanofiltration process, the exclusion of heavy metals and phytosanitary products could be assured due to the ability of these membranes to reject di- and multivalent ions and small solutes. Reverse osmosis may also be used in the final concentration. The solvent could be reused for the extraction process from wastes. Adsorption and rejection of solutes during ultrafiltration of polyphenol from grape must increase fouling resistance and reduce transmission of polyphenols to the permeation. Optimization of the process concerns the type of the membrane (polarity), pressure, pH adjustment, and volume reduction factor depending on the origin of the extracts.

Polypropylene (PP)

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Polypropylene (PP), also known as polypropylene, polypropene, propene polymers, propylene polymers, and 1-Propen, is a thermoplastic polymer made from the monomer propylene and unusually resistant to many chemical solvents, bases, and acids. The chemical structure of PP is shown in Fig. 1. The relative orientation of each methyl group relative to the methyl groups in neighboring monomer units has a strong effect on the polymer's ability to form crystals. It is the second most important plastic with revenues expected to exceed US\$ 145 billion by 2009.



Polypropylene (PP), Fig. 1 Basic structure of polypropylene

It is well known for its low cost, lightness, recyclability, easy processability, and good mechanical properties (for instance, high rigidity, impact strength, heat resistance, and durability). It is widely used in applications of packaging and labeling, textiles, stationery, plastic parts and reusable containers, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. Also it is widely used to high volume plastic materials. It becomes more resistant to high temperatures and stiffer at lower density when not subjected to mechanical stress, which is the main advantage of its application in construction materials and automobile industry, as well.

Based on the tacticity, it is divided into three types: isotactic polypropylene, atactic polypropylene, and syndiotactic polypropylene (Ray and Robert 2010). PP was first synthesized to a crystalline isotactic polymer by Giulio Natta as well as by the German Karl Rehn in March 1954. This pioneering discovery led to a large-scale commercial production of isotactic polypropylene by the Italian firm Montecatini from 1957 onward. Syndiotactic PP was also first polymerized by Natta and his coworkers. Crystals, such as Ziegler-Natta catalysts and metallocene catalysts, is very important for synthesis. The most representative manufacturing processes to produce PP are hydrocarbon slurry or suspension, bulk (or called bulk slurry), and gas phase. Hydrocarbon slurry uses a liquid inert hydrocarbon diluent in the reactor to facilitate transfer of propylene to the catalyst, the removal of heat from the system, the deactivation/removal of the catalyst, as well as dissolving the atactic polymer. The range of grades that could be produced was very limited. Bulk uses liquid propylene instead of liquid inert hydrocarbon diluent. The polymer does not

dissolve into a diluent, but rather rides on the liquid propylene. The formed polymer is withdrawn and any unreacted monomer is flashed off. Gas phase uses gaseous propylene in contact with the solid catalyst, resulting in a fluidized bed medium.

Melt processing of PP can be achieved via extrusion and molding. Common extrusion methods include production of melt-blown and spun-bond fibers to form long rolls for future conversion into a wide range of useful products, such as face masks, filters, diapers, and wipes. The most common shaping technique is injection stretch, which is used for parts such as cups, cutlery, vials, caps, containers, housewares, and automotive parts such as batteries. The related techniques of blow molding and injection stretch blow molding are also used, which involve both extrusion and molding (Moore 1996).

It is used in the manufacturing piping systems. This material is often chosen for its resistance to corrosion and chemical leaching. Many plastic items for medical or laboratory use can be made from PP because it can withstand the heat in an autoclave. Biaxially oriented PP is used to make a wide variety of materials including clear bags. It is widely used in ropes, distinctive because they are light enough to float in water. It is also used as alternative polyvinyl chloride as insulation for electrical cables. It is used in particular roofing membranes as the waterproofing top layer of single-ply systems as opposed to modified-bit systems. It is used for the production of stationery folders, packaging, and storage boxes. Expanded PP is a foam form of PP, used in model aircraft and other radio-controlled vehicles by hobbyists. PP is used in the manufacture of loudspeaker drive units.

PP can be fabricated into PP membranes with absolute pore size ratings and used in various aqueous and organic solvent samples for applications of aqueous and organic solvent, ion chromatography, total digest for heavy metals, separator materials for batteries, and so on. The Environment Working Group classifies PP as of low to moderate hazard. PP is recyclable and has the number 5 as its resin identification code.

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Polypropylene Membrane

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Polypropylene membrane (PP membrane) is one of the most important polymeric membranes and is widely used in the removal of bacteria, beer and wine clarification, wastewater treatment, oil–water separation, blood oxygenation, as a separator for batteries, etc. PP membrane is a hydrophobic membrane and it is flexible, durable, unbreakable, nontoxic, and uniform in strength. The polypropylene membrane has excellent chemical resistance, acid and alkali resistance, and solvent resistance. It can be used at high temperatures and to ensure a good filter velocity and flux. It could suitably support for cell growth, filter medium, solution disinfection, and other biological research because of no media loss and contamination. It has a long using life and good thermal stability. It is also good for gas filtration field.

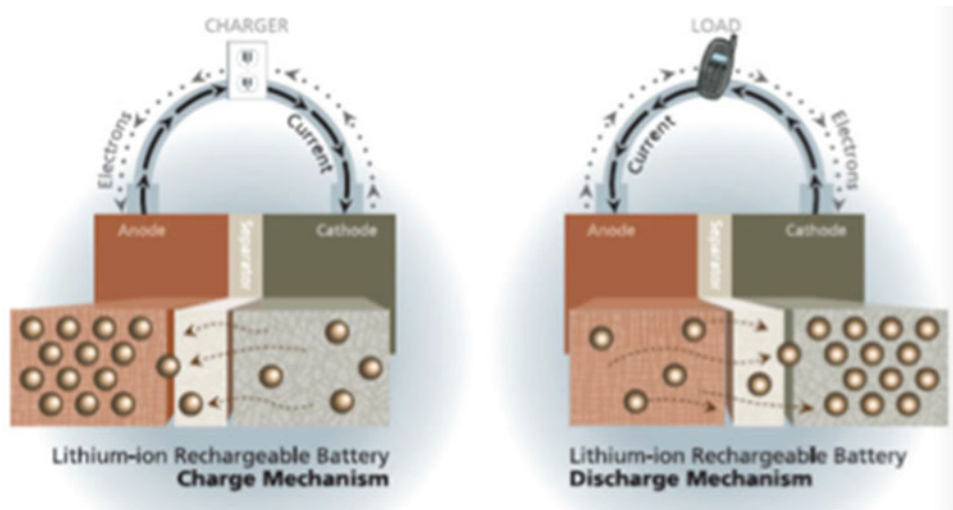
When PP membrane is extruded and stretched in both the machine direction and across machine direction, it is called biaxially oriented polypropylene (abbreviated as BOPP). Biaxial orientation increases strength and clarity. BOPP membranes often have a thickness of 20 μm . Most of BOPP membranes are manufactured by conventional longitudinal–transverse sequential biaxial stretching method. In conventional longitudinal–transverse sequential biaxial stretching method, polymer is melted by an extruder, filtered, extruded from a slit die, and wound around a

metal drum to prepare a cooled and solidified unstretched membrane. The unstretched membrane is passed between rolls of different rotating speeds and is stretched in the longitudinal direction. The membrane is then fed into a tenter, is stretched in the transverse direction, and is heat-set, cooled, and wound. This process is the typical process for manufacturing biaxially stretched polypropylene membranes (Masuda et al. 2010). BOPP is widely used as a packaging material for packaging products such as snack foods, fresh produce, and confectionery. It is easy to coat, print, and laminate to give the required appearance and properties for use as a packaging material. This process is normally called converting. It is normally produced in large rolls, which are slit on slitting machines into smaller rolls for use on packaging machines.

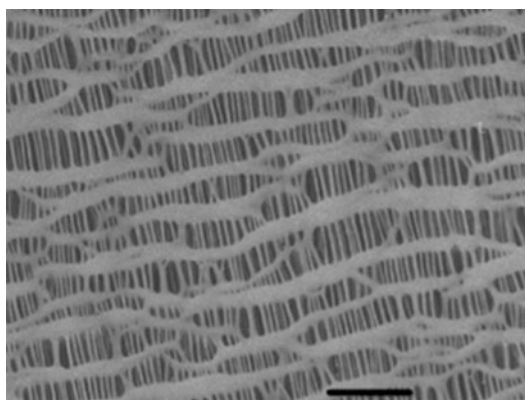
Casting PP (abbreviated as CPP) membrane, also known as the non-stretched PP membrane, is produced by casting PP membrane extrusion process. Relative to the polyethylene membrane, polyester membrane, and PVC membrane, CPP membrane is not only less expensive but also has a high gloss, has good flatness, has aspect of the performance balance, is easy to seal, and has easy processing of metal and other characteristics. And CPP membrane may be corona treated aluminum, printing or with other materials; therefore, CPP membrane is widely used as food, daily necessities, and electronic packaging materials.

PP membrane is used as battery separator that is among the most highly engineered and critical components of lithium battery systems. They provide a barrier between the anode and the cathode while enabling the exchange of lithium ions from one side of the battery to the other. Separation mechanism of PP membrane for lithium-ion battery is shown in Fig. 1.

Because of fundamental engineering and economic advantages over competing separation technologies, PP membranes are also used for CO_2 capture from power plant emissions. PP membrane with 71 % porosity is also used as proton exchange membrane fuel cell. It is prepared in supercritical CO_2 with high solubility to obtain a porous having high porosity and mechanical strength without forming a high amount of



Polypropylene Membrane, Fig. 1 Separation mechanism of PP membrane for lithium-ion battery (Celgard)



Polypropylene Membrane, Fig. 2 Field emission scanning electron micrographs (magnification, 20,000) for PP membrane. Scale bar is 1 μm

wastewater (Kim et al. 2005). A typical field emission scanning electron micrograph for PP membrane is shown in Fig. 2.

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Polyvinylidene Fluoride (PVDF)

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PVDF is a semicrystalline polymer with the repeating unit of $-\text{CH}_2-\text{CF}_2-$. The commercial PVDF is generally produced by the polymerization of vinylidene difluoride in emulsion or suspension. PVDF chains can crystallize into at least four distinct phases or forms, which are α (form II), β (form I), γ (form III), and δ (form IV). PVDF has excellent resistance to most solvents, acids, bases, and heat. It can be dissolved in some strong polar aprotic solvents, e.g., dimethylacetamide (DMAc), dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), triethyl phosphate (TEP), etc. It has a low critical surface tension of 25–28.5 dyn/cm. The melting temperature is around 160–180 °C, and the glass transition temperature is around 41 °C. It can be used in the coating, insulator, chemical, semiconductor, medical, and defense industries, lithium-ion batteries, as well as porous membranes for filtration and purification, etc. (Liu et al. 2011).

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Polyvinylidene Fluoride Membranes

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Polyvinylidene fluoride (PVDF) membrane usually refers to a porous microfiltration or ultrafiltration membrane with the pore size distribution of 0.01–0.4 μm . Typically, it is fabricated via phase inversion including immersion precipitation and thermally induced phase separation, besides non-solvent assisted thermally induced phase separation (Nat-ips), or supercritical CO_2 (SCCO_2)-induced phase separation was recently developed for PVDF membrane formation. PVDF membranes have been extensively applied in microfiltration and ultrafiltration for general separation purposes due to its outstanding properties, such as high mechanical strength, thermal stability, chemical resistance, and high hydrophobicity, and are currently being explored as potential candidates in the applications of membrane contactor, membrane distillation, CO_2 separation, and hemodialysis. PVDF membrane can be produced and assembled into flat sheet or hollow fiber module, which has been widely used as a mainstream membrane bioreactor (MBR) material in wastewater treatment, submerged ultrafiltration, and pretreatment of seawater desalination (Liu et al. 2011, 2012).

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Pore Forming Agent

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High porosity, suitable pore size, and pore size distribution are essential for the usefulness of the membranes. In order to improve the membrane permeation properties, a commonly adopted approach is adding pore-forming agents (additives) in casting solution through adjusting the membrane structure. Based on the fundamental concept that the sublayer of asymmetric polymeric membrane is strongly influenced by the additives and that of their aggregates which are in the casting solution, there is always an ongoing research in exploring new suitable additives for membrane making (Mohanty and Purkait 2011). It is generally believed that pore-forming agents increase the polymer dope viscosity, create a spongy membrane structure by prevention of macrovoid formation, enhance the pore interconnectivity when added in appropriate amounts, or speed up the displacement of solvent with non-solvent in the coagulation bath, that is, enhance the liquid-liquid demixing process during precipitation of the dope solution, and therefore the formation of larger pores is favored. However, the mechanical strength of these membranes normally decreases, and pore-forming agents may eventually leach out from the resulting membrane due to their relative small sizes and their high affinity to the water (Liu et al. 2011).

Pore-forming agents are mainly divided into three categories: (1) low molecular weight inorganic salts; (2) high molecular weight additives, known as polymeric additives; and (3) other types of additives. Sometimes, mixture of more than one agent is used to provide the membrane with appropriate permeation properties:

1. Low molecular weight inorganic salts: These inorganic salts include lithium chloride (LiCl), zinc chloride (ZnCl_2), magnesium chloride

(MgCl_2), calcium chloride (CaCl_2), lithium perchlorate (LiClO_4), magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$), calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2$), and others. Currently, lithium chloride (LiCl) is commonly used. It is generally believed that ion-dipole interactions between metal ions and membrane polymers enhance the demixing process and form more and larger pores (Mohanty and Purkait 2011). With these inorganic salts added, the membrane porosity increases while the mean pore size is almost constant, which causes the water flux to significantly increase without causing an obvious drop in solution rejection.

2. Polymeric additives: Polymeric additives are normally hydrophilic in nature. These additives not only enhance the permeation properties of the membrane but also increase its hydrophilicity. Polyvinylpyrrolidone (PVP) and poly(ethylene glycol) (PEG) are commonly used and studied. The addition of polymeric membranes promotes non-solvent flux upon immersion in the coagulation bath, thus favoring the formation of large finger-like macrovoids. The membrane permeation properties change with the concentration and molecular weight of the polymer added. Generally, as the concentration of adding polymer increases, the membrane porosity and permeation flux increase. The membrane porosity and permeation flux normally also increase with increasing molecular weight of the polymer (Mohanty and Purkait 2011); Liu et al. 2011). However, the solute rejection decreases but normally does not have significant reduction.
3. Other types of additives: Other frequently used pore-forming agents include glycerol, water, alcohol, formamide, and polyethylene oxide (PEO) or the mixture of them.

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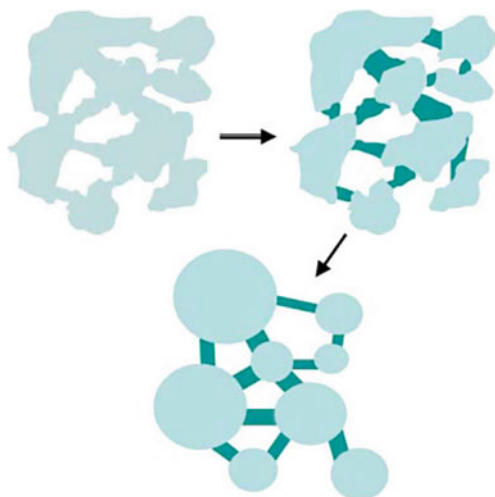
Pore Model

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Foundation for Research and Technology –
Hellas, FORTH/ICE-HT, Patras, Hellas

A model that involves a set or a network of pores to represent the void phase in the interior of porous materials. It is used in the context of pore structure characterization and as a structural basis for the prediction of transport properties. Traditionally used pore model types are the parallel pore model (Wheeler 1955), the random pore model (Wakao and Smith 1962) or dual porosity model, the cavity-neck model (Conner et al. 1983), and numerous variations. Because of the explicit representation of the void space that is offered by a pore model, major topological and geometrical features of the pore structure can be revealed or identified. The former relate mainly to pore connectivity as quantified by quantities like coordination number, genus per unit volume, etc., whereas the latter include pore shape, pore volume, pore size distribution, internal surface area per unit of volume, pore roughness, etc. These features can be extracted from individual or combined experimental techniques that can be divided into static (mercury porosimetry, gas adsorption/desorption, calorimetry, nuclear magnetic resonance, radiation scattering, wave propagation, etc.) and dynamic (liquid displacement, fluid flow). In fact, pore models play an important role in the physically meaningful and explicit interpretation of the data that are produced by these techniques. Once a pore model is set up, investigations of transport phenomena in the interior of porous materials in a direct manner are greatly facilitated for the prediction of effective transport properties and for the identification of underlying mechanisms. Notable examples are diffusion of single species and multicomponent mixtures, single and multiphase flow, heat and ion conduction, convective diffusion and conduction, transport in catalytic or non-catalytic fluid-solid reaction systems accompanied by pore

structure evolution, etc. In the presence of chemical reaction, as, for instance, in membrane reactors, access to and removal from the reaction front of reactants and products are affected significantly by the pore structure features, and the use of a pore model that is temporally changing is highly appreciated. The study of wetting phenomena is also greatly facilitated by the employment of pore models both for the purpose of structure characterization and for the theoretical modeling of capillary phenomena during immiscible and miscible displacement in porous media with the objective to predict percolation and breakthrough conditions. Thanks to this direct usefulness of pore models in the identification of structural features and in the prediction of transport properties and the fact that membrane separation is based on selective transport, pore models enjoy strong utilization in membrane science and engineering. More specifically, pore models are used for the understanding of the role of the membrane pore structure in the target separation process, for the elucidation of the relationship between structure and transport, and for the design of new or modified membranes for specific separations. Pore models are a major design component in numerous membrane processes, including, most notably, gas separation, ultrafiltration, microfiltration, pervaporation, membrane contactors, membrane distillation, etc. Flux equations at the individual pore scale and at the pore network scale have been developed (Maxwell-Stefan equations, dusty gas equations) that describe the relationship between driving forces and resulting fluxes of the different species (Jackson 1977). The former include gradients of species concentration, partial pressure, chemical potential, pressure, temperature, etc. For pore networks that can be characterized adequately by a constant or a mean coordination number, effective medium treatments are available that homogenize the transport property of a distributed pore size network and with the help of the smooth field approximation can offer an excellent estimate of the overall transport of the pore structure (Burganos and Sotirchos 1987). In the case of variable connectivity of the pore network,



Pore Model, Fig. 1 Pore segment identification process to produce a cavity-neck model

standard network solutions are available in the form of numerical algorithms that practically express the continuity condition at pore intersections (Fig. 1).

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Pore-Through-Flow Catalytic Membrane

► Contactor-Type Catalytic Membrane Reactor

Porous Functional Membranes

Bijay P. Tripathi

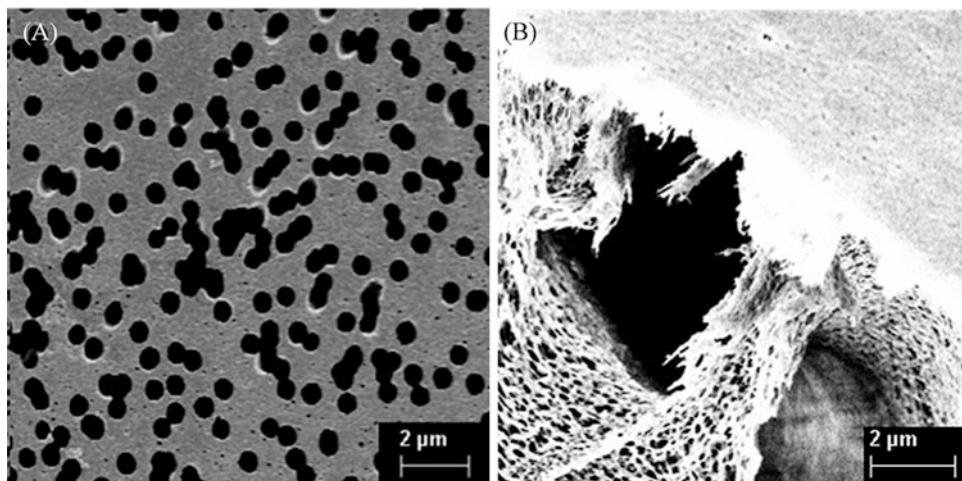
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Germany

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments. The main advantages of membrane technology as compared with other unit operations in (bio)chemical engineering are related to this unique separation principle, i.e., the transport selectivity of the membrane (Ulbricht et al. 2006). With an annual market growth rate above 10 %, membranes now play a leading role in many industries including water treatment, energy, electronics, health care, and agrobusiness. The importance of membrane technology is emphasized by the fact that one of the major challenges of this century is the provision of safe drinking water for a growing population. The most promising solutions to this problem which are environmental and energy friendly could come from new filtration membranes tailored at nanoscale (Elimelech et al. 2011). In the past decade, membrane separations have gained high technical relevance in a wide range of applications, from water purification to medical applications. Membrane-based filtration processes, such as reverse osmosis and ultra- or nanofiltration, are commonly used in desalination, waste-water treatment, and power generation. Major problems associated with membrane-based separation processes include fouling (chemical and biological) and high pressure loss, which decrease the efficiency of the filtration, decrease membrane lifetime, and increase operation costs. Main challenges for the development of novel filtration membranes are a narrow and adjustable pore-size distribution and a thin barrier layer so that the trade-off between

high selectivity and high flux could be overcome. Several polymeric materials are being studied in an effort to improve membrane performance. Generally, filtration membranes are derived from membrane-forming materials with better stability and durability such as polyamide, poly(ether sulfone), polyvinylidene fluoride, polyethylene terephthalate, polytetrafluoroethylene, etc. Membranes based on these polymeric materials are mainly prepared by either phase inversion process or track-etching process. The scanning electron microscopy image of track-etched and phase inversion membrane is given in Fig. 1.

However, despite many benefits, these materials suffer with relatively high hydrophobic nature which is a considerable limitation in water filtration application because it does not allow water permeation at significant rate. Suitable functionalization and surface modification have been reported as material design strategies for increasing the hydrophilicity of these membranes. To increase the hydrophilicity, various additives are used in the fabrication of membranes that can be broadly categorized into the polymeric additive groups of polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG), and weak solvents such as glycerol. The addition of PVP and PEG has become a standard method to obtain “hydrophilized” membranes. To avoid the leaching-out problem, covalent grafting and cross-linking with additives have been suggested (Tripathi et al. 2014; Yang and Gleason 2012).

Recently a new type of functional and environmental stimuli-responsive membranes has been proposed, which can control the water permeability and solute rejection responding to various stimuli, such as pH, salt, temperature, solute, special chemical substances, and so on. With nanoscale pores, high porosity, narrow pore-size distributions, ability for selective functionalization, and tunable chemical and mechanical properties, block copolymers hold tremendous potential as robust, efficient, and highly selective separation membranes (Tripathi et al. 2013; Nunes and Car 2013). Block copolymers are

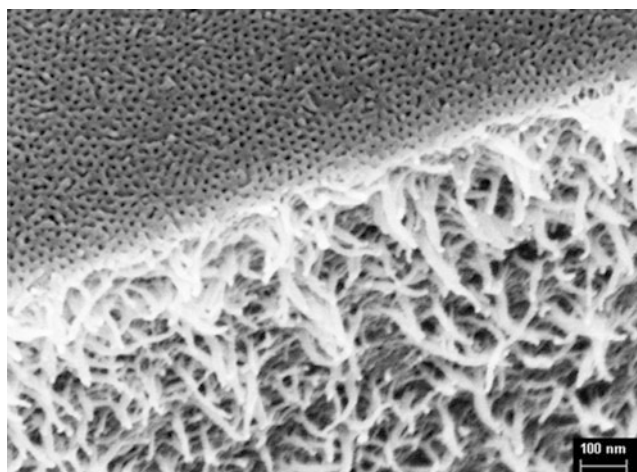


Porous Functional Membranes, Fig. 1 Scanning electron microscopy image of porous polymeric membranes: (a) polyethylene terephthalate track-etched membrane and

(b) asymmetric ultrafiltration membrane of polyether sulfone (Tripathi et al. 2014)

Porous Functional Membranes,

Fig. 2 Isoporous polystyrene-poly 4-vinyl pyridine blocks copolymer membrane (Tripathi et al. 2013)



promising materials for fabricating high throughput and improved amphiphilic filtration membranes. The self-assembly of block polymers can produce membranes with narrow pore-size distributions and high porosities, an advantage over current filtration membranes with polydisperse pore sizes. Although nanoporous membranes based on block copolymers offer great chemical tunability, limitations in thermal stability, mechanical performance, and solvent resistance can thwart even broader applications (Fig. 2).

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Porous Membranes

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Porous membranes consist of a solid matrix with defined holes or pores which have diameters ranging from less than 2 nm to more than 20 μm (Strathmann et al. 2006). The separation of solutes by porous membranes is mainly a function of molecular size and membrane pore size distribution (Baker 2004). These membranes are used to separate colloid particles or large molecular weight solutes from the solvent. High selectivity can be obtained when the solute size or particle size is relatively larger than the pore size of the membrane. Using the definition of pore size as adopted by the IUPAC (Sing et al. 1985), the porous membrane with average pore diameters larger than 50 nm is classified as macroporous, and those with average pore diameters in intermediate range between 2 and 50 nm are classified as

mesoporous. Membrane with average pore diameters between 2 and 0.2 nm is classified as microporous. Below 0.2 nm, membranes are classified as nonporous (or dense). Table 1 summarizes membrane processes based on macroporous, mesoporous, and microporous membranes and their separation mechanism and transport model.

Based on the type of structure, membranes can be distinguished in symmetric, in which the pore diameters do not vary over the membrane cross section or asymmetric. In this case, the pore diameters increase from one side of the membrane to the other side.

A wide range of inorganic materials such as ceramics, glasses, metals, or organic including different classes of polymers can be used to fabricate porous membrane. The material selection and pore size of the membranes depend on the application for which it would be used.

The membrane conformation can be flat sheet assembled in spiral wound module or tubular. On the basis of the diameters, tubular membrane is classified as follows (Mulder 1996):

1. Hollow fiber membrane (diameter <0.5 mm)
2. Capillary (diameter 0.5–5 mm)
3. Tubular (diameter >5 mm).

The membrane performance depends on important parameters such as crystallinity of the membrane-based polymer, porous structure, hydrophobicity/hydrophilicity, surface roughness, and surface charge.

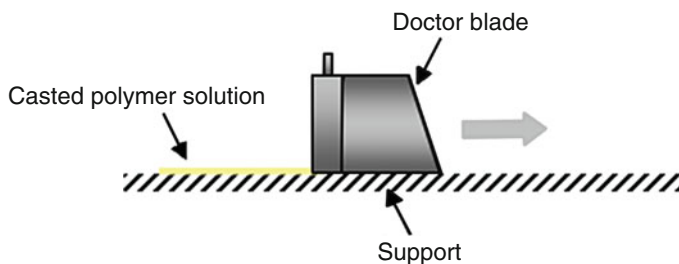
The selection of a technique for polymeric membrane fabrication depends on a choice of

Porous Membranes, Table 1 Overview of membrane processes based on porous membrane and transport model

Process	Type of membrane	Applied driving force	Separation mechanism mode of transport
Microfiltration	Macroporous	Hydrostatic pressure	Size exclusion, convection
Membrane distillation	Macroporous	Temperature difference partial pressure gradient	Diffusion
Ultrafiltration	Macroporous, Mesoporous	Hydrostatic pressure	Size exclusion, convection
Nanofiltration	Mesoporous	Hydrostatic pressure concentration gradient	Size exclusion, electrostatic interactions, solution/diffusion
Dialysis	Microporous	Concentration gradient	Diffusion
Gas separation	Microporous (or dense)	Hydrostatic pressure concentration gradient	Knudsen diffusion (solution/diffusion)

Porous Membranes,

Fig. 1 Schematic drawing illustrating the casting solution on support using doctor blade



polymer and desired structure of the membrane. The techniques commonly used for preparation of polymeric membranes include phase inversion, sintering, stretching, track etching, and template leaching (Lalia et al. 2013, Strathmann et al. 2006).

1. *Phase inversion process* can be described as a demixing process whereby the initially homogeneous polymer solution is transformed in a controlled manner from a liquid to a solid state. Figure 1 schematic drawing illustrating the casting solution on support using doctor blade is reported.

The polymer precipitation can be accomplished in several ways, namely:

- (a) *Immersion precipitation* (or non-solvent-induced phase separation NIPS). A process where a polymer solution is casted on a suitable support and then immersed in a coagulation bath containing a non-solvent, where an exchange of solvent and non-solvent takes place and the membrane is formed. The non-solvent-induced phase separation is obtained by diffusion of the solvent into the non-solvent
- (b) *Thermal precipitation* (or thermally induced phase separation TIPS). This method is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation, or freeze drying. The temperature-induced phase separation is also applicable for the preparation of porous membrane from glass mixtures and metal in combination with leaching procedure.

- (c) *Precipitation by solvent evaporation*. The polymer solution is made in a solvent or in a mixture of a volatile non-solvent and the solvent. Then the polymer solution is casted on a flat porous substrate using a doctor blade technique. When the volatile solvent evaporates from the casted solution, a thin polymer film is formed on the porous support.
- (d) *Precipitation from vapor phase*. The polymer solution is exposed to an atmosphere containing a non-solvent (typically water); absorption of non-solvent causes demixing/precipitation.

Phase inversion technique can be used to produce porous membrane with a large variety of pore size by varying the type of polymer, polymer concentration, composition of cast solution, precipitation medium, and precipitation temperature.

2. *Sintering process* allows to obtain porous membrane from organic materials and from inorganic materials. A powder of certain size particles is pressed into a film or plate and sintered just below the melting point of materials. The particles size of the powder is the main parameter determining the pore size of the membrane.
3. In the *stretching technique*, the polymer powder is extruded at temperature close to its melting point coupled with a rapid drawdown. After annealing and cooling, the extruded film is stretched perpendicular to the direction of drawing. This leads to partial fracture of the film, and relatively uniform pores are obtained.
4. In the *track etching*, a nonporous polymeric film is irradiated with energetic heavy ions leading to the formation of linear damaged tracks across the irradiated polymeric film.

Then the film is immersed in an acid or alkaline bath, and the polymer is etched away along the tracks to form uniform cylindrical pore with narrow distribution.

5. *Template leaching* is suitable for preparing porous membrane from polymers which do not dissolve in common organic solvent and also from glasses, metals, and ceramics. In this technique, a homogeneous film is prepared from a mixture of membrane material matrix and leachable component. The leachable component can be a soluble low-molecular-weight solid and liquid, or even a polymeric material. After the film has been prepared, the leachable is removed by suitable chemical treatment.

The techniques commonly used for the preparation of polymeric inorganic membranes include sintering technique and template leaching, slip casting, and sol-gel process.

1. In the *slip casting*, aluminum oxide suspension is mixed with organic polymer and poured in a mold or extruded in the desired shape as flat sheet, tube, or capillary, dried and sintered at elevated temperature. One surface of the support structure is then coated with finer particles, dried, and sintered again.
2. In the *sol-gel process*, metal oxide such as aluminum oxide is dissolved in alcohol and then hydrolyzed and precipitated by addition of excess water at elevated temperature to form a colloid solution. This solution is cooled to form gel, which is then coated on support and sintered.

Another sol-gel route involves the partial hydrolysis of metal alkoxide in alcohol solution by addition of minimum of water. The active hydroxyl groups of the alkoxide react with each other and form an inorganic/organic polymer. It is coated on the support and then dried, sintered and further cross-linked to obtain a porous structure.

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Porous Silicon

Cameron Shearer

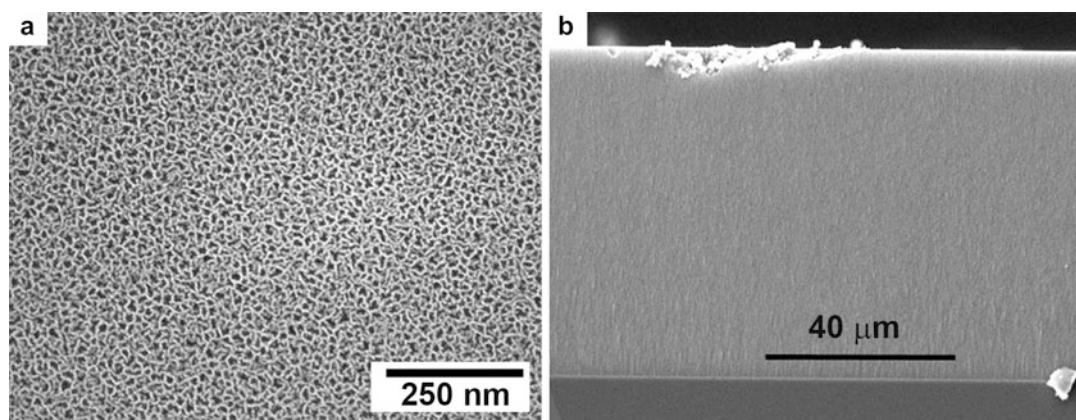
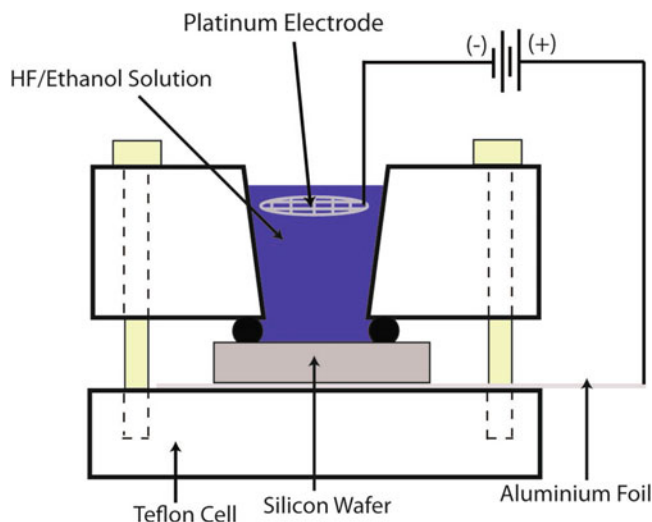
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Porous silicon (pSi), as its name suggests, is bulk silicon that has been etched by some means to form pits (pores) on its surface. Porous silicon is produced through the chemical, photochemical, or electrochemical etching of flat, crystalline silicon with fluoride solutions (Canham 1997; Schmeltzer and Buriak 2005). Galvanostatic anodization of flat silicon is the method most often employed to fabricate pSi because it provides greater reliability and selectivity to the surface produced. Aqueous hydrofluoric acid (HF) in ethanol is a common etchant used. The ethanol component is used to reduce the surface tension of the etching solution and allow full wetting of the silicon substrate (Schmeltzer and Buriak 2005). The etching process is undertaken at room temperature in a specially designed etching cell (Fig. 1) made of the fluoride-resistant Teflon. The pores produced are highly one dimensional and are of random shape (Fig. 2).

Porous Silicon,

Fig. 1 Schematic of the etching cell used for the anodic etching of silicon



Porous Silicon, Fig. 2 SEM images of (a) top-down view of porous silicon showing the irregularly shaped pores produced and (b) side-on view of porous silicon still supported on bulk silicon (at *bottom*)

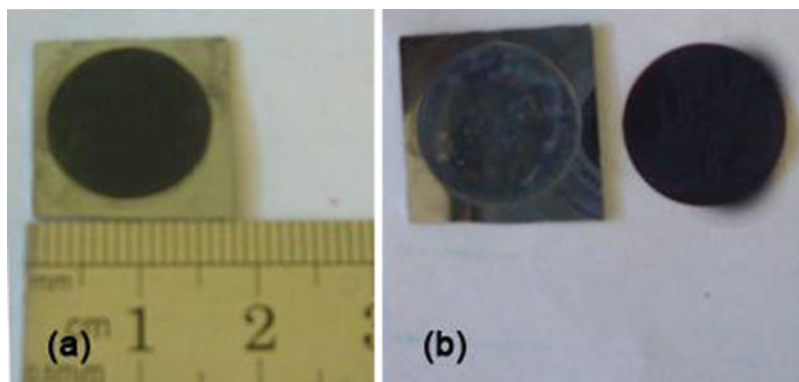
The fabricated pores formed can be in a range of tuneable sizes from micropores (<5 nm) to mesopores (5–50 nm) to macropores (>50 nm). The pore morphology is affected by the current density, silicon dopant (e.g., boron or phosphorus density), illumination, and HF concentration during etching (Canham 1997). Increasing the current density causes lateral etching and hence increasing diameter. Increasing HF concentration increases the number of F^- anions at the solution-surface interface resulting in a quicker reaction between the F^- anion and the holes, producing pores with smaller diameters and increasing porosity (Canham 1997). Etching

time affects the depth of the etch with longer times yielding deeper pores (Lehmann 2002).

HF etching of silicon yields a Si-H-terminated surface. These surfaces can be modified using a number of different chemical reactions; the most common are hydrosilylation and oxidation followed by from which a range of surface chemistries can be achieved (Schmeltzer and Buriak 2005; Jane et al. 2009). Porous silicon is an ideal biomaterial due to its biodegradability, large internal surface area, and biocompatibility that has found application in biosensing, tissue engineering, and drug delivery applications (Anglin et al. 2004; Jane et al. 2009).

Porous Silicon,

Fig. 3 Photographs of pSi membranes (a) attached to the silicon wafer and (b) lifted off the silicon wafer



Porous silicon membranes are thin layers of pSi with pores open at either end. Fabrication of pSi membranes has been achieved by etching through an entire Si wafer (Searson 1991), by etching a thin layer of pSi followed by macroscopically etching from the back side (Cruz et al. 2005), and by the “lift-off” of a pSi layer (Velleman et al. 2010). The “lift-off” procedure involves the etching of a pSi film to a desired depth followed by the electropolishing of the bottom of the film to liberate it from the bulk Si. Electropolishing is achieved by increasing the current density and/or decreasing the HF concentration. The brittle nature of pSi membranes makes them unsuitable for commercial membrane applications. However, the small pores make interesting systems for fundamental transport investigations such as gas (Solanki et al. 2004; Cruz et al. 2005) and fluid (Velleman et al. 2010, Fig. 3).

Cross-References

- [Biointerface](#)
- [Porous Silicon](#)

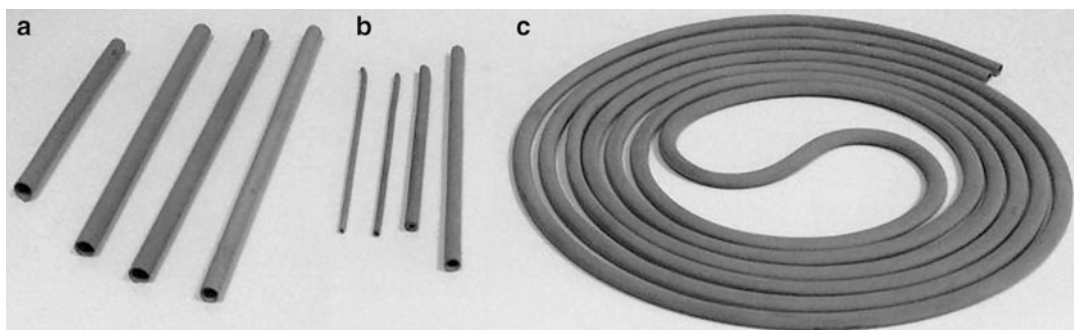
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Porous Stainless Steel Hollow Fibers

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Inorganic membranes are gaining much interest due to their high resistance against abrasion, temperature, and chemicals. They can be used for processes involving corrosive environments



Porous Stainless Steel Hollow Fibers, Fig. 1 Porous stainless steel hollow fibers produced using dry-wet spinning (a) and extrusion (b) and robotic fiber deposition (c)

and/or high temperatures, where polymeric membranes tend to fail. A subgroup of these inorganic membranes is the metallic membranes of which the stainless steel membranes are the largest group. They are not brittle, so they show a better cracking resistance; they have a high mechanical strength and allow for rapid thermal cycling. Furthermore, they can be welded or brazed, if needed, to other metallic components. These metallic membranes are mainly used as membrane supports but also have applications in microfiltration, ultrafiltration, and gas separation at high temperatures.

In contrast to polymer membranes, the most common geometry for inorganic membranes is flat sheets and tubular membranes. However, some recent developments focus on the preparation of stainless steel tubular membranes with small diameters (<5 mm), also referred to as capillaries or hollow fibers. The big advantage of these geometries is the high surface-to-volume ratio and the smaller sealing area.

Preparation

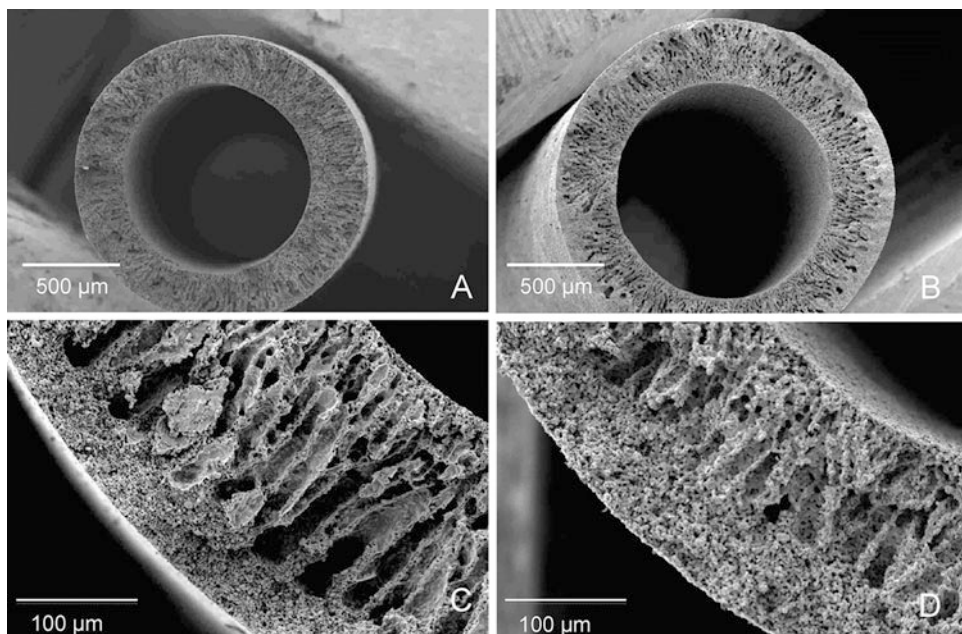
Stainless steel hollow fibers made with different processes are shown in Fig. 1. The most common techniques are either dry-wet spinning or extrusion. Both techniques start from a fine stainless steel powder which is mixed with some organic additives and/or solvents depending on the process. The mixture is then shaped into a green

hollow fiber. Afterward, the organic additives are removed during a calcination step, and the fibers obtain their final properties during a sintering step.

Spinning is a common technique to produce polymeric, ceramic, and metallic hollow fiber or capillary membranes. The technique has been originally been developed by Loeb and Sourirajan for RO membranes (Loeb and Sourirajan 1962). A mixture containing polymer, solvent, and stainless steel particles is pressed through a spinneret and subsequently immersed in a coagulation bath which contains a non-solvent. The exchange of solvent in the mixture and non-solvent in the coagulation bath induces a phase separation into a polymer-lean phase and polymer-rich phase. The polymer-rich phase solidifies and fixates the stainless steel particles.

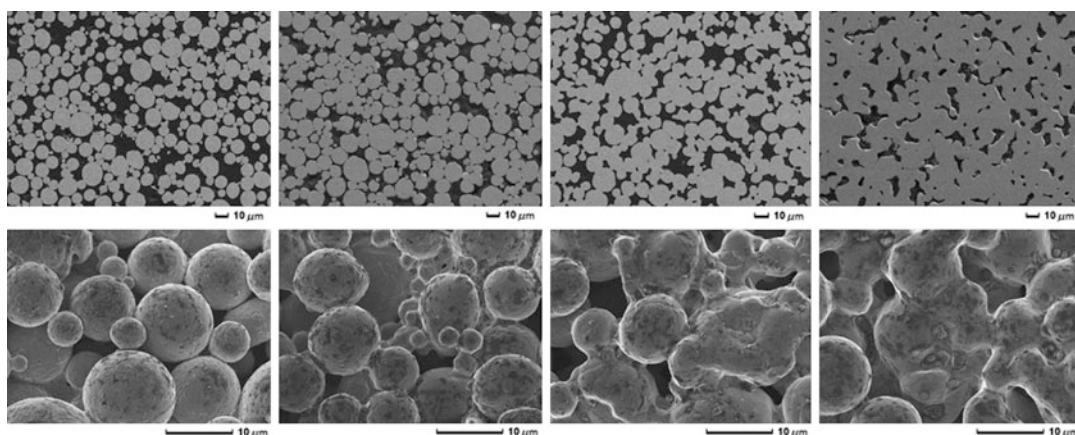
Properties

For inorganic membranes, two kinds of porous fiber morphologies can be obtained using dry-wet spinning depending upon the process parameters, i.e., fingerlike voids (large pores) and a spongelike structure (smaller pores). This is also valid for stainless steel fibers. Figure 2 shows the SEM image of stainless steel fibers containing both morphologies, the large fingerlike pores on the inside and the spongelike pores on the outside (Luiten-Olieman et al. 2011b; 2012). Their ratio can be tuned in the fibers depending on the speed of the phase inversion of the polymer mixture. This can be done by playing altering the



Porous Stainless Steel Hollow Fibers, Fig. 2 SEM images of stainless steel fiber derived from 70 wt% particle-loaded spinning mixture: (a) green compact; (b)

sintered at 1100 °C; (c) green compact, higher magnification; (d) sintered at 1100 °C, higher magnification (Luiten-Olieman et al. 2011a)



Porous Stainless Steel Hollow Fibers, Fig. 3 SEM images of the stainless steel hollow fibers sintered at different temperatures for 0.5 h. From left to right: 1000 °C,

1100 °C, 1200 °C, and 1300 °C. From top to bottom: close-up of the cross section and of the outer surface (Michielsens et al. 2013)

composition of the bore liquid and/or coagulation bad, the air-gap length, etc.

Another way to control the porosity is by adapting the heat treatment of the hollow fiber. Sintering at higher temperatures results in less porous morphologies. Figure 3 shows the effect of increasing sintering temperatures on a stainless

steel fiber. At low temperatures, almost no neck formation is visible, while an almost dense structure is obtained at high sintering temperatures.

The pore morphology and size both have an effect on the properties of the stainless steel hollow fibers. Fibers with a more open pore structure generally shows larger flux in case across the membrane.

However, the mechanical strength is generally better for the structures with spongelike morphologies and a low porosity. Therefore, depending on the intended application, a choice will have to be made between morphology with good flux properties and sufficient mechanical strength.

Cross-References

- [Bore Liquid: Solvent and Nonsolvent](#)
- [Capillary Membrane](#)
- [Coagulation Bath](#)

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- (Schrader and Jean 1988; Jean et al. 2003). These lifetime and intensity data can provide information about the molecular-scale nature of the material (Jean et al. 2003; Pethrick 1997). Typically, PALS is performed by surrounding a positron source (e.g., $^{22}\text{NaCl}$) with the sample of interest and placing it between two detectors (Jean et al. 2003). One detector is sensitive to the photon that is produced when the positron forms, and the other detector is sensitive to the photon that is emitted when the positron annihilates (Jean et al. 2003). The signals from these detectors can be processed and sorted to determine the length of time between each formation and annihilation event (Schrader and Jean 1988; Jean et al. 2003; Pethrick 1997). This information can be further processed and analyzed to determine the average lifetime of each positron species that forms and annihilates in the sample (Schrader and Jean 1988; Jean et al. 2003; Pethrick 1997). Additionally, the intensity or the concentration of each positron species that forms and annihilates in the sample can be determined, and these data can provide additional information about the nature of the sample.

The lifetime of a positron depends on the positron's electronic state and its environment (Schrader and Jean 1988; Jean et al. 2003; Pethrick 1997). When a positron combines with an electron to form positronium, para-positronium (p-Ps) is formed if the spin states of the electron and positron are parallel, and ortho-positronium (o-Ps) is formed when the spin states of the electron and positron are antiparallel (Pethrick 1997). The lifetime of p-Ps is 0.125 ns, and in molecular media the average o-Ps lifetime typically falls in the range of 0.5–5 ns (Pethrick 1997). The lifetime of free positrons in molecular media is typically around 0.4 ns (Pethrick 1997).

Because the average lifetimes of free positrons and o-Ps in molecular media are sensitive to their environment, these lifetimes can be related to the size of molecular-scale void space or free volume in the media (Pethrick 1997; Mallon 2003; Ju et al. 2010; Xie et al. 2011; Hill et al. 1996, 2005; Rowe et al. 2009; Tao 1972; Eldrup et al. 1981; Zhang et al. 2012; Freeman and Yampolskii 2010; Liao et al. 2011; Chen

Positron Annihilation Lifetime Spectroscopy (PALS)

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Synonyms

PALS

Positron annihilation lifetime spectroscopy is used to determine the average lifetimes and intensities of positron species in molecular media

et al. 2012). The small size of positrons and positronium allows PALS to probe angstrom-scale void spaces in molecular media (Pethrick 1997; Hill et al. 2005). Additionally, in some materials, the intensity of o-Ps can be related to the concentration of void spaces in the material, but this relationship can be disrupted by the chemical nature of the sample (Pethrick 1997; Xie et al. 2011; Kobayashi et al. 2009). This feature is useful for studying nonporous membranes for both gas and liquid separations because free volume in these materials is related to the diffusion of small molecules through the material (Ju et al. 2010; Xie et al. 2011; Hill et al. 1996, 2005; Rowe et al. 2009; Zhang et al. 2012; Freeman and Yampolskii 2010; Chen et al. 2012; Yampol'skii et al. 2006; Cohen and Turnbull 1959; Matteucci et al. 2006).

Cross-References

- [Polymeric Membrane Characterization by PALS](#)
- [Positron Annihilation Spectroscopy](#)

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Positron Annihilation Spectroscopy

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Synonyms

[Positron annihilation technique](#)

Positron annihilation spectroscopy (PAS) is a tool for studying positron and positronium chemistry

(Schrader and Jean 1988; Jean et al. 2003; Pethrick 1997). Positrons, which are positively charged electrons, interact with molecular media to form a variety of different electronic states, and these species subsequently annihilate (Schrader and Jean 1988; Jean et al. 2003). Positronium, which is a neutral atom composed of a positron and an electron, can also interact with molecular media and subsequently annihilate (Jean et al. 2003). In addition to forming positronium, positrons can also interact with molecules in molecular media (Schrader and Jean 1988; Jean et al. 2003). Positron-electron annihilation produces photons, and PAS measures the energies and momenta of these photons (Pethrick 1997). Furthermore, these photons can be detected as single events, and this information can be used to determine the photon's emission time and the lifetime of the positron or positronium atom (a separate characteristic photon resulting from formation of the positron can also be detected) (Jean et al. 2003; Pethrick 1997). Because the electronic state of the positron and its environment in molecular media affect the annihilation process, PAS can provide information about the electron density and electron momentum of the annihilation site (Schrader and Jean 1988; Jean et al. 2003; Pethrick 1997; Hill et al. 2005; Tao 1972; Eldrup et al. 1981).

PAS is performed by irradiating a sample with positrons. Typically, the positron source for PAS is ^{22}Na (often prepared as a salt, such as $^{22}\text{NaCl}$) (Jean et al. 2003; Pethrick 1997). Other positron-emitting isotopes or beam-line sources, however, can be used to perform PAS (Jean et al. 2003; Rowe et al. 2009). One benefit of a beam-line source as opposed to an isotope source, such as ^{22}Na , is the ability to control the energy of the incident positron, which in turn, determines the positron's depth of penetration into the sample (Jean et al. 2003; Rowe et al. 2009). Therefore, PAS can be used to probe material properties as a function of depth from the surface (typically ranging from a few nanometers to several micrometers) when an appropriate beam-line source is available (Jean et al. 2003; Rowe et al. 2009).

Three techniques, positron annihilation lifetime spectroscopy (PALS), Doppler broadening

spectroscopy (DBS), and angular correlation of annihilation radiation (ACAR), are commonly used to perform PAS although other specialized techniques exist (Jean et al. 2003; Pethrick 1997). While DBS and ACAR provide information about positron annihilation mechanisms, PALS can provide information about the molecular-scale structure of molecular media (Pethrick 1997). As a result, PALS is often used to characterize molecular-scale voids (i.e., free volume) in membranes (Pethrick 1997; Hill et al. 2005; Rowe et al. 2009; Yampol'skii et al. 2006; Park et al. 2007; Ju et al. 2010; Xie et al. 2011; Tung et al. 2009; Zhang et al. 2012).

Cross-References

- [Polymeric Membrane Characterization by PALS](#)
- [Positron Annihilation Lifetime Spectroscopy \(PALS\)](#)

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Positron Annihilation Technique

► Positron Annihilation Spectroscopy

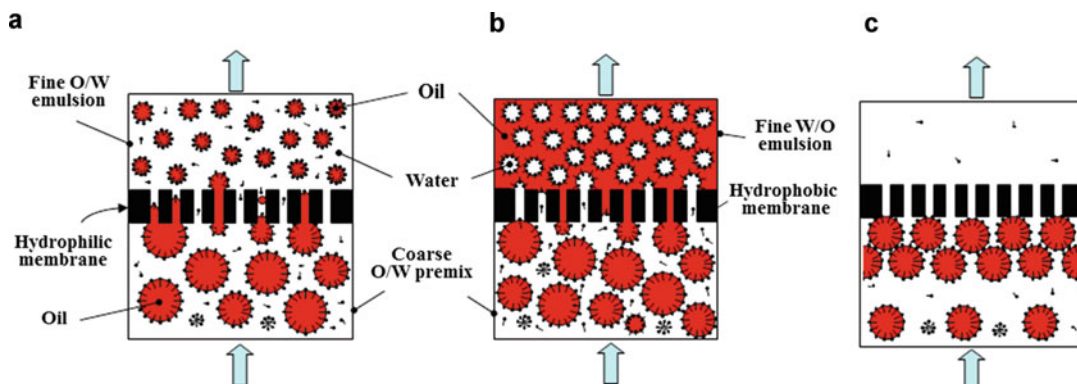
Premix Membrane Emulsification

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Premix membrane emulsification (PME) is a homogenization process based on passing

coarsely emulsified mixture of two immiscible liquids (pre-emulsion) through a microporous membrane (Suzuki et al. 1996) or porous bed of particles (Yasuda et al. 2010). In conventional PME (Fig. 1a), the dispersed phase does not wet the membrane surface ($\theta > 90^\circ$), and thus, hydrophilic and hydrophobic membranes are needed to manufacture oil-in-water (O/W) and water-in-oil (W/O) emulsion, respectively. If the pressure difference is lower than the capillary pressure in a pore (Fig. 1c), the droplets are retained by the membrane, which leads to emulsion separation rather than homogenization (Koltuniewicz et al. 1995).

If the membrane surface is wetted by the dispersed phase of the original emulsion ($\theta < 90^\circ$) and suitable surfactants are present in both liquid phases, a phase inversion may occur during homogenization (Fig. 1b), leading to the formation of W/O emulsion from an O/W premix or vice versa (Suzuki et al. 1999). The main advantage of PME with phase inversion is that a fine emulsion with high disperse phase concentration (over 80 vol.%) can be produced from a low-concentration premix. Using a membrane wetted by the middle phase of the multiple emulsion, W/O/W and O/W/O emulsion can be inverted into a W/O or O/W emulsion, respectively. In the case of inversion of W/O/W emulsion (Fig. 2), a lamellar structure is formed inside the pores consisting of surfactant bilayers

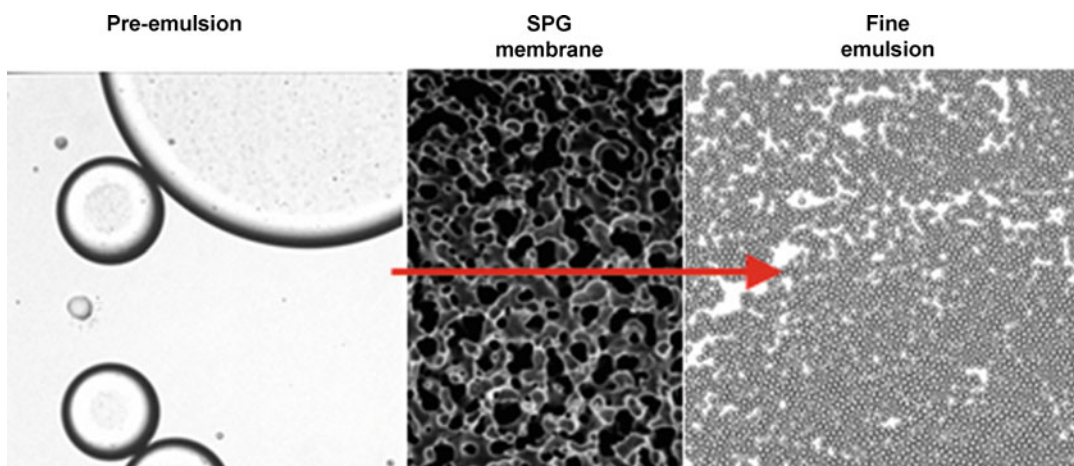
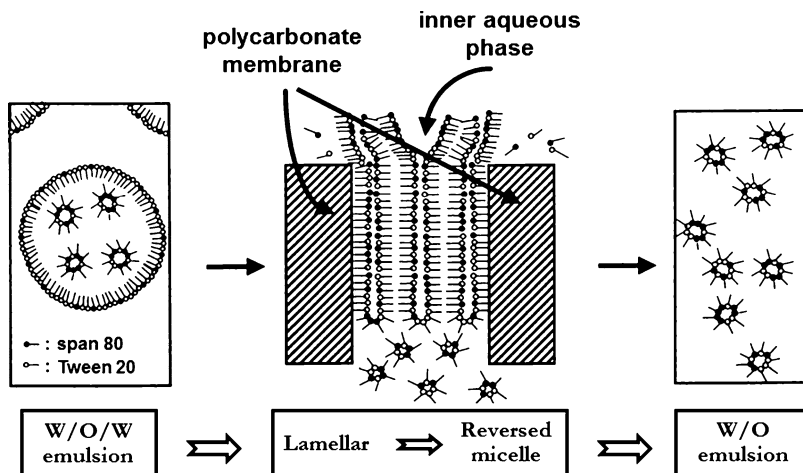


Premix Membrane Emulsification, Fig. 1 Pressure-driven membrane processes with oil-in-water pre-emulsion: (a) PME without phase inversion ($\Delta P > P_{cap}$, $\theta > 90^\circ$) (Suzuki et al. 1996). (b) PME with phase inversion

($\Delta P > P_{cap}$, $\theta < 90^\circ$) (Suzuki et al. 1999). (c) Phase separation ($\Delta P < P_{cap}$, $\theta > 90^\circ$) (Koltuniewicz et al. 1995). θ is the contact angle at which a dispersed-phase/continuous-phase interface meets the membrane surface

Premix Membrane Emulsification,

Fig. 2 Phase inversion of W/O/W emulsion into W/O emulsion using hydrophobic polycarbonate membrane. The original W/O/W emulsion consisted of liquid paraffin (middle phase), Span 80 (a hydrophobic surfactant), and Tween 20 (a hydrophilic surfactant), and a pore size was 3 or 8 μm (Hino et al. 2000)



Premix Membrane Emulsification, Fig. 3 PME using SPG membrane. The droplet size in the product emulsion was 9 μm and the membrane pore size was 10.7 μm (Vladislavljević et al. 2004)

separated by aqueous films. The aqueous films are ruptured at the pore outlets forming reversed micelles stabilized by mixed surfactants. This W/O emulsion can be redispersed into an aqueous surfactant solution to form a redispersed W/O/W emulsion containing more uniform internal droplets than the original W/O/W emulsion (Hino et al. 2000).

In order to achieve additional droplet size reduction and improve droplet size uniformity, emulsion can repeatedly be passed through the same membrane (Vladislavljević et al. 2004). Repeated membrane homogenization was originally developed for homogenization of large lipid vesicles using track-etch polycarbonate filters

(Olson et al. 1979). The advantages of premix over direct membrane emulsification are in smaller droplet sizes and higher droplet throughputs that can be achieved for the given pore size but at the expense of lower degree of monodispersity.

The droplet size in premix ME is determined by the membrane pore size, transmembrane flux, physical properties of the dispersed and continuous phase and emulsion formulation. Small droplet size in the product emulsion is favored by small membrane pore sizes, high transmembrane fluxes, and low interfacial tensions between the dispersed and continuous phase (Vladislavljević et al. 2004, 2006). The membranes used in PME are shirasu

porous glass (SPG) membrane (Fig. 3), polymeric microporous membranes (Hino et al. 2000), and microsieves (Nazir et al. 2011).

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Pressure Decay Method

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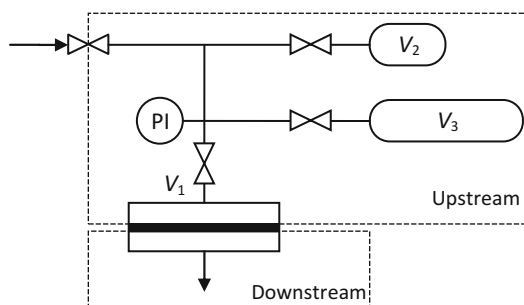
Pressure decay method is one of the standard experimental techniques for characterization of

membranes and membrane materials in terms of sorption, diffusivity, or permeance; this method has a rather high sensitivity (Ferrari et al. 2010; Mulder 1996). The principle of this method is based on estimation of amount of molecules sorbed or permeated through the membrane by monitoring of pressure decay in a chamber with a constant known volume, where the membrane is placed. The amount of gas or vapor sorbed by membrane material at a given pressure is determined by the difference between initial and actual pressures; for sorption experiments, the actual pressure is equilibrium one. Mass flow through the membrane is determined by monitoring of pressure decay in a chamber above the membrane with a constant volume (upstream side) in time. This technique is more commonly used for measurement of gas transport due to higher values of compression coefficients, and the schematic view of this experimental setup is shown in Fig. 1.

If the volume of upstream side V_{upstream} is already calibrated and known, the mole flow of the gas J through the membrane surface A over the time period Δt can be described as a function of pressure drop in the following equation with approximation of ideal gas law:

$$J(\text{mole}/\text{m}^2 \cdot h) = \frac{V_{\text{upstream}} \cdot \Delta p}{R \cdot T \cdot A \cdot \Delta t}$$

where R is universal gas constant and T is temperature. The method accuracy can be improved by avoiding any temperature fluctuations (e.g., in



Pressure Decay Method, Fig. 1 Schematic view of experimental setup to measure gas flow with pressure decay method: *PI* pressure indicator, V_1 calibrated volume of pipelines and fittings, V_2 calibrated vessel volume, V_3 calibrated vessel volume

case of gas expansion) during single measurement and proper selection of highly sensitive and accurate pressure indicator(s) for required pressure range.

The drawback of this method is that the driving force across the membrane is continuously changing during the single test since the upstream side is isolated from the gas supply. However, it is possible to consider a constant transmembrane pressure difference if the pressure drop for single test is negligible in comparison with absolute pressure in upstream side. On the other hand, such a pressure drop value should be sufficiently high enough to eliminate the undesired effect of temperature fluctuation and instrumental noise. From this end, the upstream side typically includes two or more vessels with different calibrated volumes (see Fig. 1), so the overall volume can be adjusted by connecting one of the vessels or its combination to the main line in order to measure the membranes with different permeance at the same experimental setup within desired experimental error.

Pressure decay method is also used as a rapid test for evaluation of the integrity of micro- and ultrafiltration membranes as well as membrane modules (AWWA Staff 2005). The upper side of wetted membrane is pressurized with a gas, which is below its bubble point pressure. Broken membrane or not proper sealing would be indicated by noticeable rate of pressure decay. Recently, a new self-calibration technique based on principles of pressure decay method was proposed for the express determination of liquid flux through flat-sheet membranes in a pressure range of 30–150 bar (Grekhov et al. 2012).

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Pressure Retarded Osmosis (PRO) for Energy Generation

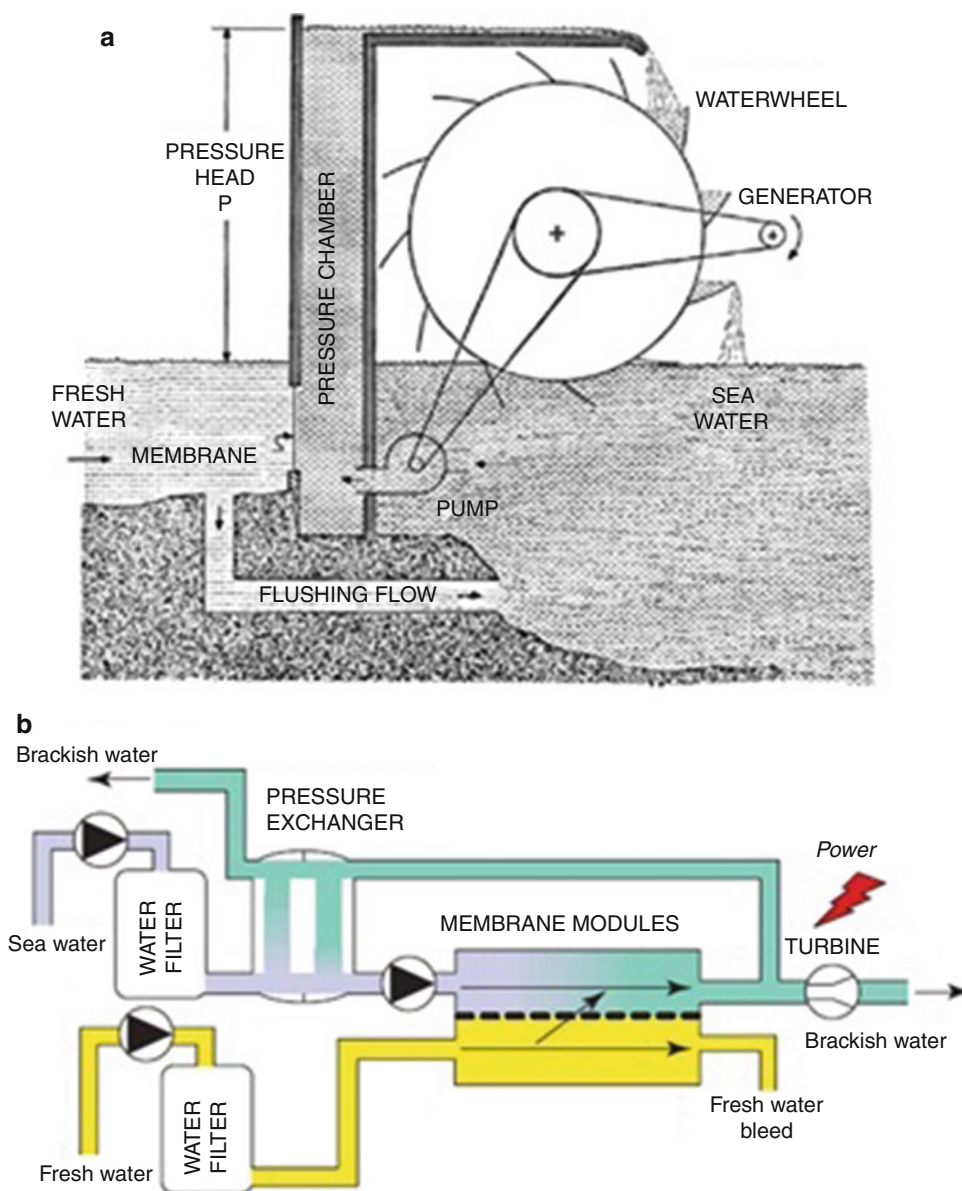
► Membranes for Blue Energy

Pressure-Retarded Osmosis

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During the past decades, the world's constantly growing population and energy demand had brought the great challenges to thoroughly search for alternative energy resources. The mixing of fresh and saline water releases a tremendous energy that can potentially be used for power generation (Pattle 1954). In fact, there are huge resources where freshwater meets saline water that have not been explored. It has been estimated that this potential energy resource can generate 200 TWh/year of electric power, creating more than 10 % for the world energy demand (Achilli and Childress 2010). The energy released from the mixing of fresh- and saltwater can be captured by a membrane process, the so-called pressure-retarded osmosis (PRO).

PRO utilizes osmotic pressure (π) as the driving force for water to transport across a semipermeable membrane from a water source with lower salt concentration (low π) to a source with higher salt concentration (high π). The flow of water from the dilute source increases the volumetric flow at the concentrate side, and this flow can be used for driving a turbine to generate electricity (see Fig. 1).

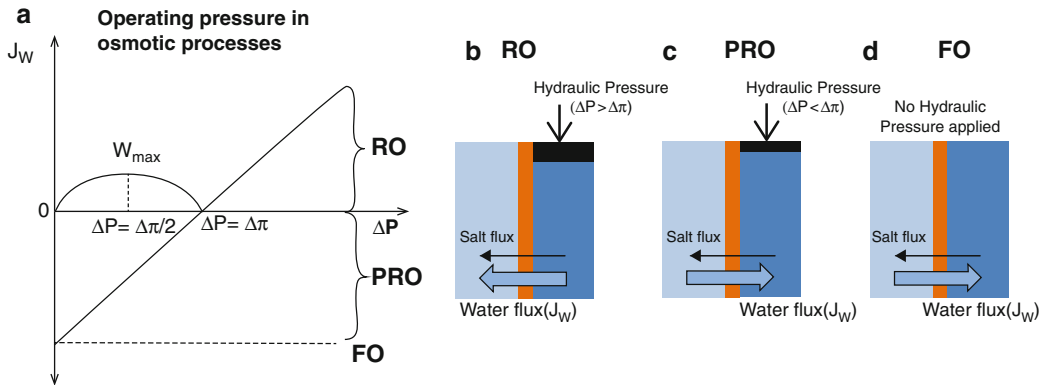


Pressure-Retarded Osmosis, Fig. 1 Schematic diagram of (a) the first osmotic salination energy converter, proposed by Norman in 1974 (Norman 1974), and

(b) the first prototype PRO, designed and operated by Statkraft (Oslo, Norway) (Skilhagen et al. 2008)

There are three osmotic pressure-related membrane processes: reverse osmosis (RO), forward osmosis (FO), and PRO. Regarding applied hydraulic pressure (P), the required pressure to retain osmotic equilibrium, PRO can be viewed as the transition process from FO to RO as shown in Fig. 2.

RO membranes require a mechanical strength that can withstand the high pressure applied, while FO and PRO operate at much lower pressures, thus no special strength is strictly required. Typical RO membrane is thus designed to have a thin selective layer on top of thick support layer. The membrane performance and solute retention



Pressure-Retarded Osmosis, Fig. 2 (a) Illustration of the magnitude of the operating pressure and water flux of a membrane in the ideal case and direction of water and salt flux for (b) RO, (c) PRO, and (d) FO process

are determined by the top-skin layer. The support only provides the mechanical strength to the RO membranes and the liquid flows through it under the influence of a pressure gradient. On the other hand, for FO and PRO, the physical and chemical nature of support layers (e.g., porosity, tortuosity, and hydrophilicity) play an equally important role as the skin layer. The presence of unwetted pores or gas trapped inside the pores of the support in FO or PRO can cause internal concentration polarization (ICP) and dramatic flux reductions. Moreover, membranes suitable for FO and PRO are required to possess high salt rejection to prevent reverse salt passages and ICP and to be thin, highly porous, and hydrophilic in nature to favor high water fluxes and good transport of leakage salts. Additional mechanical strength (just enough to resist the installed operating pressure) is required for PRO.

The ideal water permeation rate across the membrane is a linear function of both osmotic pressure difference and the applied hydraulic pressure:

$$J_w = A(\Delta\pi - \Delta P)$$

where J_w is water flux and A is the water permeability constant. The power generated by a PRO system is expressed by

$$W = J_w \Delta P = A(\Delta\pi - \Delta P) \Delta P$$

It is clear that the power generated by PRO is a parabolic function of in which the maximum

value is estimated to be at $\Delta P = \Delta\pi/2$. Thus, the maximum power generated from PRO ($W_{max} = A\Delta\pi^2/4$) is proportional to the water permeability constant and the square of the osmotic pressure difference.

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Principal Component Analysis (PCA)

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PCA can be considered in many ways as the basis for multivariate analysis. It is probably the most widespread multivariate statistical technique used

in chemometrics. Perhaps the most famous early paper was by Pearson in 1901. However, the fundamental ideas are based on approaches well known to physicists and mathematicians for much longer, namely, those of eigen-analysis. In fact, some school mathematic syllabuses teach ideas about matrices which are relevant to modern chemistry. It is generally accepted that the revolution in the use of multivariate methods took place in psychometrics in the 1930s and 1940s of which Hotelling's paper is regarded as a classic. Natural scientists of all disciplines, from biologists, geologists, and chemists, have caught on to these approaches over the past few decades. Within the chemical community, the first major applications of PCA were reported in the 1970s and form the foundation of many modern chemometric methods (Wold 1987).

PCA can be described as a way of identifying patterns in data and expressing the data in such a way as to highlight their similarities and differences. PCA is a powerful tool to analyze patterns in data with high dimension. The main advantage of PCA is the possibility to compress the data: it means reducing the number of dimensions without loss of information. This approach has been recognized as a useful technique in data reduction, modeling, outlier detection, variable selection, classification, and prediction as well (Brereton 2003).

PCA provides an approximation of a data matrix $\mathbf{X}$, in terms of the product of two small matrices called $\mathbf{T}$ and $\mathbf{P}$ as reported in the following:

$$\mathbf{X} \approx \hat{\mathbf{C}} \cdot \hat{\mathbf{S}} = \mathbf{T} \cdot \mathbf{P}$$

where $\mathbf{T}$ is the scores, and ideally has the same dimensions as $\mathbf{C}$, and $\mathbf{P}$ the loadings ideally having the same dimensions as $\mathbf{S}$ (Brereton 2003). Each scores' matrix consists of a series of column vectors and each loadings matrix a series of row vectors, the number of such vectors equaling the rank of the original data matrix.

The mentioned matrix $\mathbf{X}$ has an order $n \times k$, in which n represents the experimental rows (also called objects) and k which corresponds to the

factors comprising the measurements made on the objects (Wold 1987).

The reduction of the dimension is performed by linear combination, named principal components (PCs). The first principal component covers as much of the variation in the data as possible. The second principal component is orthogonal to the first and covers as much of the remaining variation as possible and so on. The numbers of PCs are less than or equal to the number of original variables. The quantity of PCs is determined by using the eigenvalue.

It is easy to convert the PCs from number into graph by using statistical data and modern computers. As a matter of fact, it is common to think PCs geometrically as much as numerically, and often PCs are treated as much as objects in an imaginary space than mathematical entities. By using commercial software, it is possible to obtain a large number of graphs rapidly. Score plots and loading plots are the main way to visualize the PCs, helping to appreciate interrelationships between different variables as well as detect and interpret sample patterns, clusters, similarities, or differences (Brereton 2003).

Applications of this approach are immersed in different fields such as neuroscience, image processing, authentication, and differentiation of wines with different geographical origin (Saavedra et al. 2011), as well as for the identification of adulterate products. Applications of this approach in membrane processes have been reported with successful results. Typical examples are related to the analysis of membrane bioreactor fouling behavior (Maere et al. 2012), the prediction of ternary gas permeation through synthesized PDMS membranes (Ghadimi et al. 2010), and the analysis of nanofiltration of single and mixed salt solutions (Hesampour et al. 2010). Despite the advantages of this approach, PCA applied for the analysis of membrane processes is still in its infancy.

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Principle of Biocatalytic Membrane Reactors (BMR)

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Synonyms

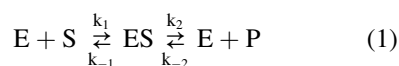
Biocatalytic membrane reactors; Biochemical membrane reactors; Biological membrane reactors

Biocatalytic membrane reactors are systems where the biocatalyst is loaded/immobilised to membrane and the bioconversion occurs at the membrane level, so that the membrane functions as support for the biocatalyst, contactor between reaction components, reactor and separation unit.

The most common type of biocatalyst used in biocatalytic membrane reactors is enzyme. Whilst some enzymes are not very specific, many will catalyse only one reaction involving only certain substrates. Enzyme specificity is thought to be a consequence of its elaborate three-dimensional conformation which allows formation of the “active site,” a hydrophobic cavity responsible

for the catalytic ability of the enzyme. Binding to create the substrate-enzyme complex is in general due to weak attractive forces. Although a little controversial, the notion of active sites and the enzyme-substrate complex are universally accepted and form the starting point for most theories of enzyme action.

The relative chemical equation is:



The mathematical expression of the kinetic behaviour of enzymes is commonly known as Michaelis-Menten equation:

$$V_0 = \frac{V_{\max}[S]}{K_M + [S]} \quad (2)$$

The Lineweaver-Burke equation is obtained by rearranging the M-M equation in linear form:

$$\left[\frac{1}{V_0} \right] = \frac{K_M}{V_{\max}} \left[\frac{1}{[S]} \right] + \frac{1}{V_{\max}} \quad (3)$$

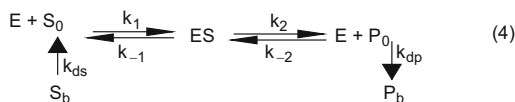
By plotting $\frac{1}{V_0}$ versus $\frac{1}{[S]}$ data, a straight line is obtained, where the intercept to y axis is $1/V_{\max}$ and the slope is $K_m/V_{\max}$. From this graph, it is easy to estimate K_m and $V_{\max}$.

When the enzyme is immobilised in a matrix such as a polymeric membrane, the observed reaction rate depends upon the reagent transport and intrinsic catalytic activity of the enzyme. The Michaelis-Menten constant is often larger for an immobilised enzymatic system than for the corresponding homogeneous system.

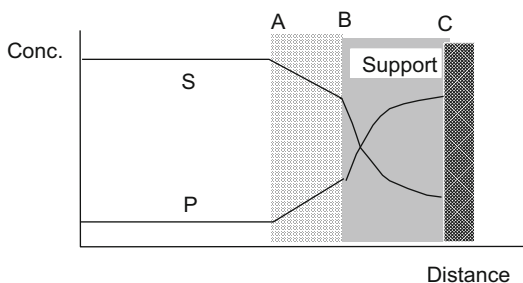
The use of Lineweaver-Burk plots with immobilised enzymes to determine apparent values for $V_{\max}$ and K_m is very common. For a kinetically controlled reaction, a straight line is obtained. A linear extrapolation to the axes allows the apparent values of these parameters to be accurately determined.

In the presence of diffusional limitations, the Michaelis constant's apparent value obtained by extrapolation of the Lineweaver-Burk plot is usually larger than that for the soluble form. Under these conditions, the Michaelis-Menten equation

can no longer account for the overall kinetics. In general, the kinetic mechanism for an immobilised enzyme can be simply represented as follows:



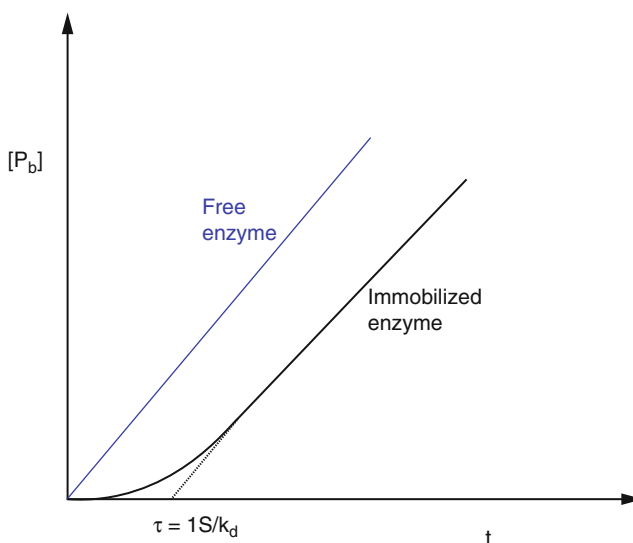
where S_0 and P_0 are the concentrations next to the immobilised enzymes, whilst S_b and P_b are the concentrations in the bulk phase. The constant k_{ds} is related to the diffusion of substrate from the bulk to the enzyme, and k_{dp} is related to the diffusion of product from the immobilised enzyme to the bulk phase. In Fig. 1, the concentration gradients for substrate and product through



Principle of Biocatalytic Membrane Reactors (BMR),
Fig. 1 Concentration gradients through immobilised enzyme matrix

Principle of Biocatalytic Membrane Reactors (BMR),

Fig. 2 Reaction catalyzed by free and immobilised enzyme



porous supports containing immobilised catalysts are schematised. The gradients in regions A–B are due to diffusion in the outer diffusion liquid film. The gradients in regions B–C are due to the joint effects of diffusion and reaction.

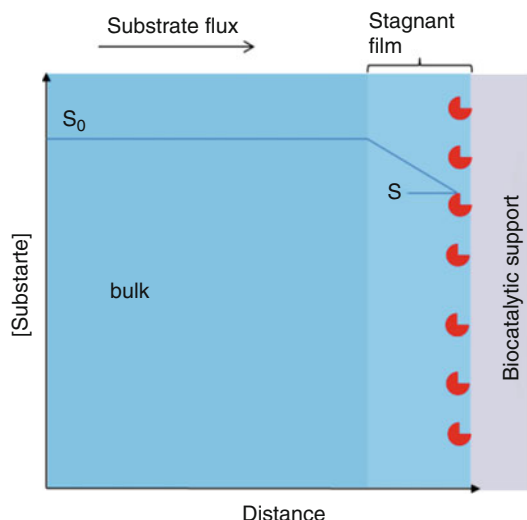
For reactions monitored by measuring the increase of product in the bulk phase, the profile of product concentration as a function of time will present a time lag due to the diffusion of substrate from the bulk to the enzyme-loaded membrane and diffusion of product from the immobilised enzyme to the bulk phase (Fig. 2).

Depending on the place where the enzyme is immobilised, there are two main cases:

- Biocatalytic membrane reactors with enzyme immobilised on the membrane surface
- Biocatalytic membrane reactors with enzyme immobilised within the membrane porous matrix

Biocatalytic Membrane Reactors (BMR): Enzymes Immobilised on the Membrane Surface

In order to permit the catalytic action of immobilised enzyme, the substrate must diffuse from the bulk to the biocatalytic support, and the products must diffuse away into the bulk solution.



Principle of Biocatalytic Membrane Reactors (BMR), Fig. 3 Schematic representation of transport for catalyst immobilised on the surface of insoluble support

In this particular case, a stagnant film (or Nernst diffusion layer, thus called by biochemists) forms around the particle through which the substrate molecules must diffuse to reach the surface. Thus, the surface concentration is less than the bulk concentration; the reaction proceeds less rapidly than the bulk substrate concentration would suggest (Fig. 3).

The Michaelis-Menten equation shows that an increase of K_m also corresponds to a decreased reaction rate; therefore, the diffusional effect is not surprising. The flux of substrate from bulk to immobilised interfaces is given by $J_s = k_s(S - S_0)$.

where J_s is the flux (moles per unit time per unit area), S and S_0 are the substrate concentration in the bulk phase and at immobilised enzyme interface, and k_s is the mass transfer coefficient.

At steady state, at the interface, the mass transfer of substrate must be counterbalanced by the consumption rate of the substrate. Then, assuming

that Michaelis-Menten equation applies at systems immobilised on the surface,

$$k_s(S - S_0) = \frac{V_{\max}[S]}{K_M + [S]} \quad (5)$$

The following is a dimensionless variable:

$$Da = \frac{V_{\max}}{k_s S_0} \quad (6)$$

Known as the Damköhler number, it has an important physical meaning, being a ratio between the maximum reaction rate and maximum mass transfer rate.

When $Da \ll 1$, the maximum transfer rate is much larger than the maximum reaction rate, which means that the system works at low mass transfer resistance. This is the case known as reaction-limited regime. This means that the system is kinetically controlled and the equation

$$V_{kin} = \frac{V_{\max}[S]_b}{K_M + [S]_b} \quad (7)$$

can be assumed.

When $Da \gg 1$, the reaction rate is larger than the mass transfer, which means that the mass transfer resistance is large and it is the limiting process. This is the case known as diffusion-limited regime and $V_{diff} = k_s[S]_b$.

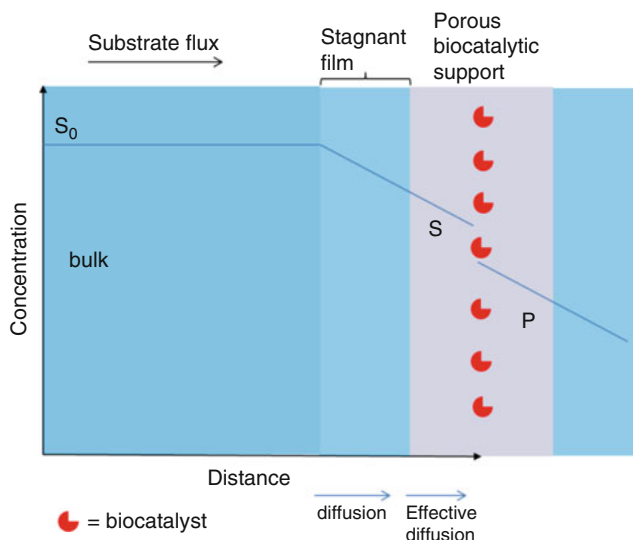
The Damköhler number can be interpreted as the ratio of the slope of V_{kin} to that of V_{diff} , evaluated by plotting V versus $[S]_b$. If the slope of V_{diff} ($= k_s$) is less than that of V_{kin} ($= V_{\max}/K_M$) at $S_b = 0$, then $Da [= (V_{\max}/K_M)/(k_s)] > 1$ and the reaction is diffusion controlled; whilst, in the opposite case, the reaction is kinetically controlled.

The influence of mass transfer on the overall reaction is usually represented using the effectiveness factor, η , defined as:

$$\eta = \frac{\text{Observed reaction rate}}{\text{Rate that would be observed in absence mass transfer resistance}} \quad (8)$$

Principle of Biocatalytic Membrane Reactors (BMR),

Fig. 4 Concentration profiles through catalytic porous matrix



When $\eta \leq 1$, it means that the mass transfer resistance is large and the effect is a reduction of the observed activity of the catalyst.

For Da approaching zero (very slow reaction relative to maximum mass transfer rate), η approaches 1. This means that for the reaction-limited regime, the observed reaction kinetics can be approximate to the intrinsic reaction kinetics.

Biocatalytic Membrane Reactors (BMR): Enzyme Immobilised Within the Porous Matrix

Immobilisation of enzymes has a significant influence on their kinetics. This can be due to both structural changes of the biocatalyst and changes in the microenvironment around the enzyme.

The activity of the immobilised enzyme is governed from the chemical-physical properties of the microenvironment instead of that one of the bulk phase. When enzymes are immobilised within the internal surface of porous supports (Fig. 4), calculation of the observed substrate conversion rate needs evaluation of the concentration profile of the substrate within the diffusion layer.

With respect to the biocatalytic system in which biocatalyst is immobilised on the surface support, in this case, the additional resistance to substrate diffusion given by the porous matrix must be considered.

The effective diffusion coefficient (D_{eff}) and the local rate of substrate conversion (V) differ conceptually from their counterpart in solution, and important quantitative difference can also arise.

Substrate porosity, tortuosity and restricted diffusion influence their value. Porosity, ϵ_p , is given by the ratio of “area of support/area of pores”; only part of the support is void and available for diffusive transport, while most part is occupied by solid. Tortuosity, ϵ , is a factor representing the fact that the pore network is complex and not straight, therefore, diffusion occurs changing direction continuously. The tortuosity factor is assumed to be in the range of 1.4 to 7. Pores can have very small diameter, similar to substrate molecular dimensions and lead to a situation of restricted diffusion (expressed as K_p/K_r , roughly estimated as $[1 - r_{substrate}/r_{pore}]^4$).

Taking into account these considerations, the effective diffusion coefficient can be written as:

$$D_{eff} = D_{S_0} \frac{\epsilon_p}{\tau} \frac{K_p}{K_r} \quad (9)$$

In the 1930s, Thiele, Damköhler and Zeldovitch studied the influence of *diffusion within porous catalysts* upon reaction kinetics. They considered the example of a planar membrane containing enzyme distributed uniformly throughout. The result of combining the steady-state diffusion

equation with the applicable kinetics rate expression, the Michaelis-Menten equation, is:

$$Deff \frac{d^2[S]}{dx^2} - \frac{V_{max}[S]}{K_m + [S]} = 0 \quad (10)$$

where D_{eff} is the effective diffusivity, $[S]$ is the substrate concentration, V_{max} is the maximum velocity of the reaction, and K_m is the Michaelis constant, which means that, at steady state, the substrate diffusion rate through the porous support containing enzyme is equal to the conversion rate.

The values V_{max} and K_m are those which characterise the kinetics expression for the microenvironment within the porous structure.

A useful parameter to evaluate if an immobilised reaction system is limited by kinetics or mass transport is the Thiele modulus, ϕ , given by:

$$\phi = L \left(\frac{V_{max}}{D_{eff} \cdot K_m} \right)^{1/2} \quad (11)$$

which has the physical meaning of a *reaction rate/diffusion rate*.

As a final remark, it should be noted that, as for the enzyme in solution, immobilised enzyme kinetics may differ from the single substrate irreversible Michaelis-Menten model. In the case where the intrinsic kinetics is inhibited by substrate, if the substrate at the external phase is higher than the substrate concentration giving the maximum reaction rate, it happens that the local reaction rate inside the support is larger than that at the external phase. In this specific situation, it is possible to observe an effectiveness factor higher than unity. Other frequent cases are heterogeneous systems, such as the substrate solubility limit and the liquid-liquid interface.

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Principle of Dialysis

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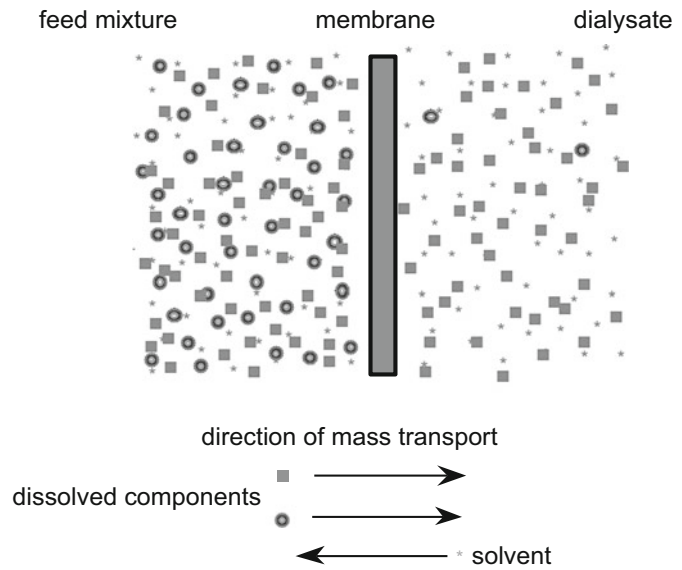
Synonyms

Mass transport in dialysis

Dialysis is carried out under isobaric conditions, and there is no temperature or electrical potential gradient. The principle of the process is depicted in Fig. 1 (Strathmann et al. 2006).

Principle of Dialysis,

Fig. 1 Schematic drawing illustrating the principle of dialysis with two neutral components of different size



The schematic drawing shows a liquid solution containing a solvent and molecular components of different molecular weight or size, referred to as feed solution separated by a membrane from the solvent referred to as dialysate or “stripping” solution. Due to the driving force of a concentration difference, the components will diffuse through the membrane from the feed solution to the dialysate. Their fluxes through the membrane and the separation are determined by the diffusion rate in the membrane matrix.

There are different forms of dialysis depending on the constituents of the feed solution and the structure of the membrane. The most simple form is the dialysis of neutral components, i.e., the components in the solution do not carry any electrical charge.

Dialysis Mass Transport of Components Carrying No Electric Charges

The mass flux in dialysis of a mixture, which contains neutral components, only can be expressed by the phenomenological equation, which can then be related to Fick’s law by several approximations.

For a membrane and a feed solution with uncharged components, the flux of a component at constant temperature and pressure is given by:

$$J_i = -L_i \frac{d\mu_i}{dz} = -L_i RT \frac{d \ln a_i}{dz} = -L_i RT d \ln C_i \gamma_i \quad (1)$$

Here J is the flux, L is a phenomenological coefficient, μ is the chemical potential, a is the activity, C is the concentration, γ is the activity coefficient, z is the directional coordinate perpendicular to the membrane, and the subscript i refers to a component.

Assuming that the activity coefficient is 1 and replacing the phenomenological coefficient by the diffusion coefficient leads to:

$$J_i = L_i \frac{RT}{C_i} \frac{dC_i}{dz} = D_i \frac{dC_i}{dz} \quad (2)$$

Equations 1 and 2 indicate that Fick’s law can describe the mass transport in dialysis with feed solutions containing neutral components adequately if there is no coupling of fluxes and if the activity coefficient of the components in the membrane is unity, which is the case in many practical applications.

Dialysis Mass Transport of Electrolytes in a Membrane Without Fixed Ions

If feed solutions with charged components, i.e., electrolyte solutions, are treated by dialysis, the electroneutrality requirement must be satisfied. For a system consisting of a membrane and solutions with various ions, the electroneutrality condition requires

$$\sum_a |z_a| C_a = \sum_c z_c C_c \quad (3)$$

Here z is the valence, C is the concentration, and the subscripts a and c refer to anion and cation, respectively.

If the membrane contains fixed ions, they must be included in the electroneutrality requirement. The fixed charges in a cation-exchange membrane are negative and in an anion-exchange membrane positive. If there is no electrical current, the conservation of the electrical charge requires that cations and anions will move in the same direction. Thus,

$$\sum_a |z_a| J_a = \sum_c z_c J_c \quad (4)$$

The concentration of the electrolyte, e.g., a single salt, is related to that of the ions by:

$$C_a = \alpha v_a C_s \text{ and } C_c = \alpha v_c C_s \quad (5)$$

Here α is the degree of dissociation of the electrolyte, v is a stoichiometric coefficient, and the subscript s refers to the electrolyte.

The stoichiometric coefficient relates the number of ions to that of the salt molecules. For a completely dissociated monovalent salt such as NaCl, α and v are 1. For a salt such as CaCl₂, v_a is 1 and v_c is 2.

In an electrolyte solution, the fluxes of the ions are the result of an electrochemical potential gradient driving force. The electrochemical potential of ions is related to that of the electrolyte by:

$$\tilde{\mu}_s = v_a \tilde{\mu}_a + v_c \tilde{\mu}_c \quad (6)$$

Here $\tilde{\mu}$ is the electrochemical potential.

Since in dialysis no external potential and no hydrostatic pressure difference is applied, the flux of the ions can be described as a function of the diffusion coefficient and the concentration gradient by Eq. 2 if the activity coefficients are assumed to be 1. However, the fluxes of the ions are related to each other by the electroneutrality requirement and the conservation of charges with the consequence that in diffusion of an electrolyte which consists of a cation and an anion with significantly different diffusivities, the faster moving ion will cause a minute charge imbalance and thus an electrical potential gradient. This potential gradient is referred to as diffusion potential, and although it might be very small, it will slow down the faster diffusing ion and speed up the slower ion so that both ions will diffuse with the same velocity.

The flux of the completely dissociated monovalent electrolyte is related to that of the ions by:

$$\begin{aligned} J_s = J_a = J_c &= -D_s \frac{dC_s}{dz} = -D_a |z_a| \frac{dC_a}{dz} \\ &= -D_c z_c \frac{dC_c}{dz} \end{aligned} \quad (7)$$

Here J is the flux, C is the concentration, D is the diffusion coefficient, z is the charge number of the ion, dz is the directional coordinate, and the subscripts s , a , and c refer to salt, anion, and cation, respectively.

Rearranging Eq. 6 under consideration of Eq. 5 gives the diffusion coefficient of the salt as a function of the diffusion coefficients of the cations and anions:

$$D_s = \frac{D_a D_c (|z_a| + z_c)}{D_a |z_a| + D_c z_c} \quad (8)$$

Combination of Eqs. 6 and 7 gives the salt and ion fluxes for a completely dissociated monovalent salt at constant temperature and pressure in an ideal solution, i.e., the activity coefficients are 1:

$$J_s = \frac{D_a D_c (|z_a| + z_c)}{D_a |z_a| + D_c z_c} \frac{dC_s}{dz} \quad (9)$$

Here J is the flux, C is the concentration, D is the diffusion coefficient, z is the charge number or the directional coordinate, and the subscripts s , a , and c refer to salt, anion, and cation, respectively.

Equation 9 describes the flux of an electrolyte as a function of the diffusion coefficients of the individual ions. This is the consequence of the electroneutrality requirement for the transport of ions which have different diffusivities because the faster moving ion will cause the buildup of a minute electrical potential gradient which will slow down the faster ion and speed up the slower ion so that at steady state both ions move with the same velocity. Therefore, an average diffusion coefficient for each ion can be defined to describe the fluxes of the different ions which are coupled by the conservation of charges and the electroneutrality condition. The average diffusion coefficient $\bar{D}$ is given by:

$$\bar{D}_c = \bar{D}_a = D_s = \left(\frac{D_a D_c |z_a| + z_c}{D_a |z_a| + z_c D_c} \right) \quad (10)$$

Equation 9 describes the transport of a single electrolyte under the driving force of a concentration or activity gradient through a membrane that does not carry any fixed charges. In this case, all ions of the electrolyte are transported in the same direction even if their diffusion coefficient is quite different. The situation, however, becomes more complex if a feed solution contains more than one

electrolyte and if the membrane carries fixed charges. In this case, certain ions might be transported against their concentration gradient.

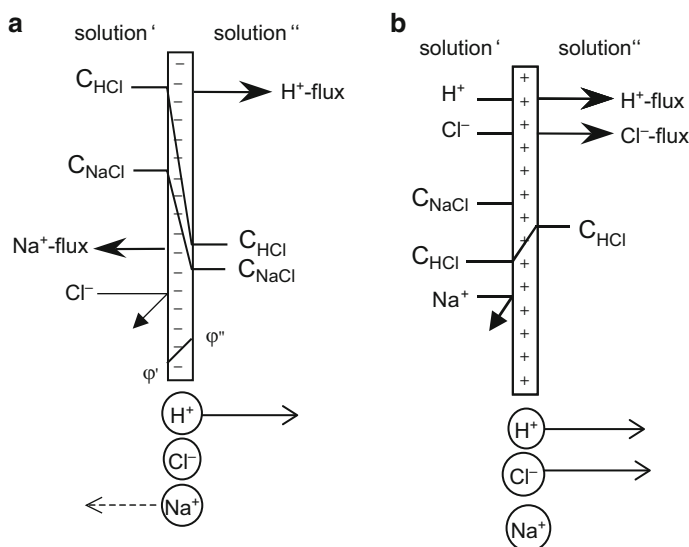
Dialysis Mass Transport of Electrolytes in Ion-Exchange Membranes

The fluxes of ions through ion-exchange membranes in dialysis are even more complex and may result in transport of certain ions against their concentration gradient as illustrated in Fig. 2. Figure 2a shows countercurrent coupled transport of H^+ - and Na^+ -ions through a cation-exchange membrane. This process is referred to as Donnan dialysis. Figure 2b depicts co-current transport of H^+ -ions and Cl^- -ions through an anion-exchange membrane.

In Donnan dialysis with a strictly permselective ion-exchange membrane, the flux of the co-ion, i.e., in Fig. 2a the Cl^- -ions, is 0, and the fluxes of the counterions, i.e., the Na^+ - and H^+ -ions, are equal but move in opposite direction. Thus, there is no net transport of electrical charges across the membrane, i.e., there is no electrical current, and the conservation of charges is fulfilled. For a system illustrated in Fig. 2a, the transport of a counterion, i.e., the Na^+ -ion, is the result of a flux of another counterion, i.e., H^+ -ion, in opposite direction under the driving force of a concentration gradient. Since no co-ions, i.e.,

Principle of Dialysis,

Fig. 2 Schematic drawing illustrating the fluxes across an ion-exchange membrane which separates two electrolyte solutions of different concentrations containing HCl and NaCl: (a) shows the fluxes through a cation-exchange membrane and represents countercurrent coupled flux, i.e., Donnan dialysis, and (b) shows the fluxes through an anion-exchange membrane and represents co-current coupled transport, i.e., diffusion dialysis



Cl^- ion, can permeate the cation-exchange membrane, the flux of the H^+ -ions must be identical to that of the Na^+ -ions. The fluxes are given by:

$$J_{\text{H}^+} = -2 \left(\frac{L_{\text{H}^+} L_{\text{Na}^+}}{L_{\text{H}^+} + L_{\text{Na}^+}} \right) \frac{RT d \ln a_{\text{H}^+}}{dz} = J_{\text{Na}^+} \quad (11)$$

The transport of Na^+ -ions due to the H^+ -ion flux results in a buildup of an activity gradient of the Na^+ -ions which is causing a back transport. When the Na^+ -ion flux caused by the activity gradient is identical to that caused by the H^+ -ion flux, equilibrium is reached, and there will be no further ion transport through the membrane. This equilibrium, which is referred to as Donnan equilibrium, is given by:

$$d \ln a_{\text{H}^+} = d \ln a_{\text{Na}^+} \quad (12)$$

The Donnan equilibrium between two solutions with different Na^+ -ion and H^+ -ion concentrations separated by a permselective cation-exchange membrane is

$$\frac{a'_{\text{Na}^+}}{a''_{\text{Na}^+}} = \frac{a'_{\text{H}^+}}{a''_{\text{H}^+}} \quad (13)$$

The superscripts ' and '' refer to the two solutions separated by the membrane.

Donnan dialysis plays an important role in water softening, and Eq. 12 determines which minimum and maximum concentrations of a counterion can be achieved by a given flux of another counterion.

Co-current coupled transport is illustrated in Fig. 2b which shows a solution containing a mixture of a salt, i.e., NaCl , and an acid, i.e., HCl , separated by an anion-exchange membrane from a solution containing no salt. The Cl^- -ion concentration in the solution containing the salt and acid mixture is assumed to be much higher than in the solution containing the acid only. Due to a concentration gradient, the Cl^- -ions permeate the anion-exchange membrane toward the solution containing the acid only. Because of the electroneutrality requirement, an anion can permeate the membrane only when accompanied by a cation. The anion-exchange membrane, however, is impermeable to cations such as Na^+ -ions, but it is to some extent permeable to H^+ -ions because

protons are transported in an aqueous solution and also in highly swollen ion-exchange membranes by a different transport mechanism (Cussler 1971). The Cl^- -ion concentration gradient across the membrane acts as driving force for the transport of H^+ -ions which are transported against their concentration gradient. The minimum concentration of the acid in the salt solution and the maximum concentration in the acid that can be achieved are given when the activity gradients of the H^+ -ion and the Cl^- -ion across the membrane are identical. The co-current transport of an anion with a H^+ -ion is of practical importance for the recovery of acids from spent pickling solutions containing the acid in a mixture with salts.

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Principle of Electrodialysis

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Synonyms

Mass transport in electrodialysis

In electrodialysis cation-exchange membranes carrying fixed negative electric charges and anion-exchange membranes carrying positive fixed charges are placed in alternating series between two electrodes. The mass transport is the result of an electrochemical potential gradient across the membrane, i.e., a gradient in the chemical and electrical potential. An electrical potential driving force is acting on charged components only and in such a way that negatively charged components, i.e., the so-called anions, migrate in the direction toward the positively charged anode and the positively charged cations migrate toward the negatively charged cathode, i.e., cations and anions move in opposite directions.

To describe the mass transport of a salt in an aqueous solution through a membrane which is used as frame of reference, three independent fluxes must be considered, i.e., the flux of the cations, the flux of anions, and the flux of the solvent. The transport of ions is the result of an electrochemical potential difference and the transport of the solvent through the membrane a result of osmotic effects and a coupling with the fluxes of the ions. Under certain conditions the solvent flux can be significant and must be taken into account.

Ion-exchange membranes carry positive or negative electrical charges fixed to a solid matrix, and they are, therefore, permselective as far as the transport of ions is concerned, i.e., the cation-exchange membranes are preferentially permeable to cations and the anion-exchange membranes are preferentially permeable to anions (Strathmann et al. 2006).

The mass transport in electrodialysis can be described by a phenomenological equation giving the flux of the individual components by:

$$J_i = \sum_k L_{ik} \frac{d\tilde{\mu}_k}{dz} = \sum_k L_{ik} \left(RT \frac{d \ln a_k}{dz} + z_i F \frac{d\phi}{dz} \right) \quad (1)$$

Here, J is the flux, L is a phenomenological coefficient, $\tilde{\mu}$ is the electrochemical potential, a is the activity, z is the valence of ionic species, F is the Faraday constant, ϕ is the electrical potential, dz is the directional coordinate perpendicular to the

membrane, and the subscripts i and k refer to the components of the mixture. Assuming an ideal solution, i.e., the activity of a component is identical to its concentration and without kinetic coupling between individual components and expressing the phenomenological coefficient by the Fick's diffusion coefficient, Eq. 1 becomes identical with the Nernst-Planck flux equation which is given by:

$$J_i = -D_i \left(\frac{dC_i}{dz} + \frac{z_i F C_i}{RT} \frac{d\phi}{dz} \right) \quad (2)$$

Here D_i is the diffusion coefficient of the component i in reference with the membrane.

The first term in Eq. 2 $D_i \frac{dC_i}{dz}$ represents the diffusion and the second term $D_i \frac{z_i F C_i}{RT} \frac{d\phi}{dz}$ the migration.

Thus, the Nernst-Planck equation is an approximation of the more general phenomenological equation.

In ion-exchange membrane separation processes such as electrodialysis, the flux of the cations through the cation-exchange membrane and the flux of the anions through the anion-exchange membrane are interdependent because of the electroneutrality requirement in the solution between the membranes.

Electrical Current and Ion Fluxes

In electrodialysis it is assumed that the total current through the membrane is carried by ions only, thus is:

$$i = \frac{I}{A} = F \sum_i |z_i| J_i \quad (3)$$

Here i is the current density, I the current, A the membrane surface, F the Faraday constant, J the flux, and z the valence, and the subscript i refers to cations and anions.

The current density i can be related to the specific conductivity κ by:

$$i = \kappa \frac{d\phi}{dz} \quad (4)$$

Here κ is the specific conductivity, φ is the electrical potential, and z is the directional coordinate.

The specific conductivity κ can be expressed by the specific electrical resistance, the equivalent conductivity, the ion migration velocity, or the ion diffusivity:

$$\begin{aligned}\kappa &= \frac{1}{\rho} = \sum_i |z_i| C_i \lambda_i = F \sum_i |z_i| C_i u_i \\ &= F^2 \sum_i |z_i| C_i \frac{D_i}{RT}\end{aligned}\quad (5)$$

Here ρ is the specific resistance, C is the concentration, F is the Faraday constant, λ is the equivalent conductivity, u is the ion migration velocity, D is the ion diffusion coefficient, R is the gas constant, T is the absolute temperature, and the subscript i refers to anions and cations.

Introducing Eqs. 4 and 5 into Eq. 3 and rearranging lead to:

$$\begin{aligned}i &= F \sum_i |z_i| J_i \\ &= F^2 \sum_i z_i^2 \frac{C_i D_i}{RT} \left(\frac{RT}{z_i C_i F} \frac{dC_i}{dz} + \frac{d\varphi}{dz} \right)\end{aligned}\quad (6)$$

Here i is the current density, C is the concentration, F is the Faraday constant, φ is the electrical potential, z is the valence, D is the ion diffusivity, R is the gas constant, T is the absolute temperature, and the subscript i refers to anions and cations.

The term $\frac{RT}{z_i C_i F} \frac{dC_i}{dz}$ has the dimension of an electrical potential gradient and represents the concentration potential, which is established between two electrolyte solutions of different concentrations. In electrodialysis this potential is established between the concentrate and the diluate solution. It represents an electromotive force, which has to be overcome by the applied electrical potential.

The Transport Number and Membrane Permselectivity

In an electrolyte solution, the current is carried by both ions. However, cations and anions usually carry different portions of the overall current. In

ion-exchange membranes the current is carried preferentially by the counterions. The fraction of the current that is carried by a certain ion is expressed by the ion transport number, which is given by:

$$T_i = \frac{|z_i| J_i}{\sum_j |z_j| J_j} \quad (7)$$

Here T_i is the transport number of the component i , J_i is its flux, and z_i is its valence and the subscript j refers to all ions involved in the charge transport.

The transport number T_i indicates the fraction of the total current that is carried by the ion i ; the sum of the transport number of all ions in a solution is 1.

The membrane permselectivity is an important parameter for determining the performance of a membrane in a certain ion-exchange membrane separation process. It describes the degree to which a membrane passes an ion of one charge and retains an ion of the opposite charge. The permselectivity of cation- and anion-exchange membranes can be defined (Spiegler 1957) by the following relations:

$$\psi^{cm} = \frac{T_c^{cm} - T_c}{T_a} \quad (8)$$

and

$$\psi^{am} = \frac{T_a^{am} - T_a}{T_c} \quad (9)$$

Here ψ is the permselectivity of a membrane, T is the transport number, the superscripts cm and am refer to cation- and anion-exchange membranes, and the subscripts c and a refer to cation and anion, respectively.

The permselectivity of an ion-exchange membrane relates the transport of electric charges by a specific counterion to the total transport of electric charges through the membrane and the transport number of the ion in the solution. An ideal permselective cation-exchange membrane would transmit positively charged ions only, i.e., for a

transport number of a counterion in a cation-exchange membrane $T_c^{cm} = 1$ is the permselectivity $\Psi^{cm} = 1$. The permselectivity approaches zero when the transport number within the membrane is identical to that in the electrolyte solution, i.e., for $T_c^{cm} = T_c$ is $\Psi^{cm} = 0$. For the anion-exchange membrane holds the corresponding relation.

The transport number of a certain ion in the membrane is proportional to its concentration in the membrane, which again is a function of its concentration in the solutions in equilibrium with the membrane phase, due to the Donnan exclusion. The concentration of a co-ion in an ion-exchange membrane can be calculated from the Donnan equilibrium. For a monovalent salt and a dilute salt solution and assuming the activity coefficients of the salt in the membrane and the solution to be 1, the co-ion concentration is given to a first approximation by:

$${}^m C_{co} = \frac{{}^s C_s^2}{C_{fix}} \quad (10)$$

Here C is the concentration; the subscripts co , s , and fix refer to co-ion, salt, and fixed ion of the membrane; and the superscripts s and m refer to membrane and solution.

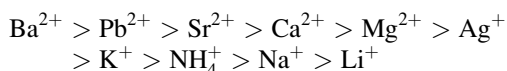
Equation 10 indicates that the co-ion concentration in the membrane is increasing with solution salt concentration and the membrane permselectivity will decrease correspondingly.

Membrane Counterion Permselectivity

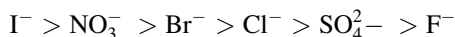
The transport number of different counterions in the membrane can be quite different. The transport rate of ions is determined by their concentration and their mobility in the membrane. The concentration of the counterions is always close to the concentration of the fixed charges of the membrane. The mobility of the ions in the membrane depends mainly on the radius of the hydrated ions and the membrane structure. The mobility of different ions in an aqueous solution does not differ very much from others. An

exception is the H^+ and OH^- ions. Their mobility is about a factor 5–6 higher than that of other ions. The exceptionally high mobility of the H^+ ion can be explained by the transport mechanism of protons. Salt ions move with their hydrate shell through the solution. Protons interact with water dipoles and form hydronium ions. They are transported in the membrane mostly via a so-called tunnel mechanism. The transport mechanism of the proton is also the reason for the high permeability of anion-exchange membranes for protons while these membranes generally have a very low permeability for salt cations. The same mechanism as the one described here for the transport of protons also holds true for the transport of hydroxide ions, and thus the permeability of hydroxide ions in a cation-exchange membrane is much higher than that of other salt anions.

The permselectivity of an ion-exchange membrane for different salt counterions is determined by the concentration and the mobility of the different ions in the membrane. The concentration of the different counterions in the ion-exchange membrane is generally also different. A typical counterion-exchange sequence of a cation-exchange membrane containing SO_3^- group as fixed charge is:



A similar counterion-exchange sequence is obtained for anions in an anion-exchange membrane containing quaternary ammonium groups as fixed charges:



Water Transport in Electrodialysis

Water transport in electrodialysis from the diluate to the concentrate process stream can affect the process efficiency significantly. If a convective flux as a result of pressure differences between flow streams can be excluded, there are still two sources for the transport of water from the diluate to the concentrate solution. The first one is the

result of osmotic pressure differences between the two solutions, and the second is due to electroosmosis which results from the coupling of water to the ions being transported through the membrane due to the driving force of an electrical potential.

Each of the two fluxes may be dominant depending on the permselectivity of the ion-exchange membrane, the concentration gradient, and the current density. In a highly permselective membrane and moderate differences in the salt concentration in the two solutions separated by the membrane, the electroosmotic flux is dominating and generally much higher than the osmotic solvent flux. In electrodialysis the water flux due to electroosmosis can be expressed by a solvent transport number which gives the number of water molecules transported by one ion:

$$J_w = {}^mT_w \sum_i J_i \quad (11)$$

Here mT_w is the water transport number, J_w is the water flux, and J_i is the flux of ions through a given membrane.

The water transport number thus is:

$${}^mT_w = \frac{J_w}{\sum_i J_i} \quad (12)$$

The water transport number refers to the number of water molecules transferred by one ion through a given membrane. It depends on the membrane and on the electrolyte, i.e., on the size of the ions, their valence, and their concentration in the solution. In aqueous salt solutions and commercial ion-exchange membranes, the water transport number is in the order of 4–8, i.e., one mole of ions transports ca. 4–8 mol of water through a typical commercial ion-exchange membrane.

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Principle of Gas Separation

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Synonyms

[Knudsen diffusion](#); [Mass transfer in gas separation](#); [Solution-diffusion mechanism](#)

Introduction

The principle of gas separation is illustrated in Fig. 1, which shows two different gas mixtures separated by a membrane. The driving force for the gas to permeate the membrane is a pressure gradient.

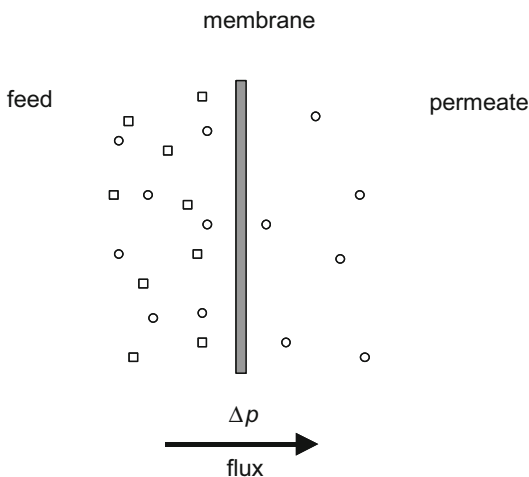
In gas separation both porous and dense membranes are used as selective barriers (Pandey and Chauhan 2001; Favre 2010; Yampolskii and Freeman 2010). In porous membranes the transport of gases is based on the so-called Knudsen diffusion. And in dense solid materials the gas transport is based on a solution-diffusion mechanism. Both the Knudsen diffusion as well as the solution-diffusion transport can result in a selective transport of gases and thus in a separation of gases. However, the extent of the separation, i.e., the separation factor is much higher in a solution-diffusion transport than in Knudsen diffusion.

Gas Separation by Knudsen Diffusion

Knudsen diffusion can be considered as viscous flow in narrow pores, i.e., pores with a diameter that is smaller than the mean free path length of the diffusing gas molecules. The mean free path length is defined as the average distance a gas molecule travels before it will collide with another gas molecule. The mean free path length of a gas molecule depends on the nature of the gas, the temperature, and the pressure. It is given by (Atkins 1990):

$$\lambda = \frac{kT}{\pi d_{\text{gas}} p \sqrt{2}} \quad (1)$$

Here λ is the mean free path length of a gas molecule, k is the Boltzmann constant, d_{gas} is the



Principle of Gas Separation, Fig. 1 Schematic drawing illustrating the principle of gas separation

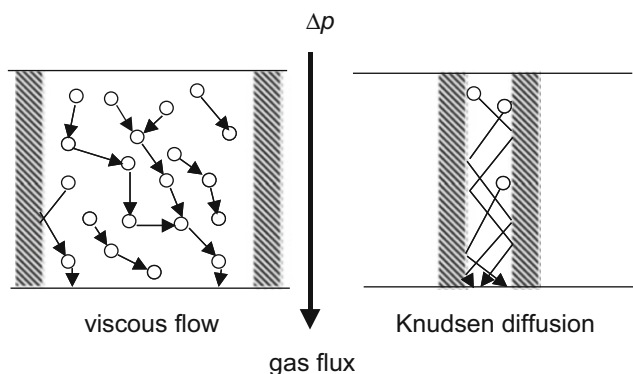
diameter of the gas molecule, and p is the hydrostatic pressure.

The difference between viscous flow and Knudsen diffusion is illustrated in Fig. 2.

The figure shows two membrane pores of different diameter with a number of gas molecules. In the pore with the larger diameter, the gas molecules have more interaction with each other than with the pore wall since the mean free path length of the molecules is much shorter than the pore diameter. In the pore with the smaller diameter, the gas molecules have more interactions with the pore wall than with each other. In the case of the larger pores, the energy loss during transportation is mainly due to the interaction of the molecule with each other. It is expressed in the viscosity of the solution. Therefore, the flux is referred to as viscous flow in which all molecules are transported with the same rate. In pores with the smaller diameter, the energy loss during the transport of the gas molecule is due to their interaction with the pore wall. The process is similar to diffusion in a homogeneous solid phase and is therefore referred to as Knudsen diffusion. Since molecules of different mole mass have different interaction energies when colliding with the pore wall they are transported with different rates. This can be utilized to separate gases which differ in their molecular weight. The mean free path length of gases at room temperature and atmospheric pressure is in the order of a couple of nanometers. This means that only membranes with a mean pore size below a couple of nanometers can separate gases due to a Knudsen diffusion mechanism. Since the free path length of a gas molecule is pressure and temperature dependent as Eq. 1 indicates,

Principle of Gas Separation,

Fig. 2 Schematic drawing illustrating viscous flow and Knudsen diffusion



membranes with larger pore diameters can be used when the process is carried out at higher temperature and low pressure.

The flux in Knudsen diffusion can be described by the following relation (Mason and Malinauskas 1983):

$$J_i = \frac{\pi n r^2 D_i^k \Delta p}{RT \tau \Delta z} \quad (2)$$

Here J is the flux through the membrane, n is the number of pores in the membrane, r is the pore radius, Δp is the pressure difference across the membrane, Δz is the thickness of the membrane, τ is the tortuosity factor, and D^k is the Knudsen diffusion coefficient.

The Knudsen diffusion coefficient is given by:

$$D_i^k = 0.66r \sqrt{\frac{8RT}{\pi M_w}} \quad (3)$$

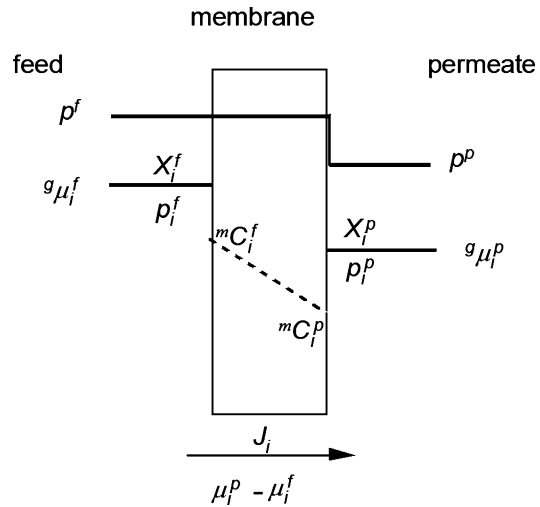
Equation 3 shows that the Knudsen diffusion coefficient of a gas molecule is inversely proportional to the square root of its molecular weight. Thus, the separation of two gases based on Knudsen diffusion is given by the ratio of the square root of the molecular weights.

$$\alpha_{j,k} \propto \sqrt{\frac{M_k}{M_j}} \quad (4)$$

Because of the Knudsen diffusion transport mechanism, the selectivity that can be achieved with porous membranes is in general rather low when gases differ only marginally in their molecular mass. Nevertheless, porous membranes are used to separate U^{235}F_6 from U^{238}F_6 . Since the selectivity is only ca. 1.0043, hundreds of stages are required to obtain a significant separation.

Gas Transport by the Solution-Diffusion Mechanism in a Polymer Matrix

Significantly higher selectivity can be obtained in homogeneous polymer membranes, where the transport mechanism is based on the solution and diffusion of the various components within the membrane phase. The mass transport in a



Principle of Gas Separation, Fig. 3 Schematic diagram illustrating the three-step transport mechanism in solution-diffusion type membranes (μ is the chemical potential, X is the molar fraction, C is the concentration, p is the partial pressure; the subscript i refers to a component and the superscripts f , p , g , and m refer to feed, permeate, gas phase, and membrane)

so-called solution-diffusion membrane is illustrated in Fig. 3. It consists of three relevant steps:

- Sorption of the various components from a feed mixture according to their partition coefficient between the gas and polymer phase
- Diffusion of the individual components within the membrane phase according to their activity gradients
- Desorption of the components from the membrane in the permeate gas phase

If viscous flow is excluded, the driving force for the mass transport of gases in solution-diffusion type membranes is the activity gradient of the permeating components within the membrane phase which can be related to the difference between the chemical potentials of the component in the feed and the permeate.

The flux across the membrane can be described again by the phenomenological equation as a function of the gradient of the chemical potential of the permeating component:

$$J_i = -L_i \frac{d^m \mu_i}{dz} \quad (5)$$

Here J is the flux, L is a phenomenological coefficient relating the flux to the corresponding driving force, μ is the chemical potential, and z is the directional coordinate perpendicular to the membrane surface, the subscript i refers to a component, and the superscript m refers to the membrane.

The chemical potential in the membrane at the membrane surface is equal to the potential in the adjacent gas phase. The change of chemical potential of a component as function of pressure and composition is given by:

$$d\mu_i = \bar{V}_i dp + dRT \ln a_i \quad (6)$$

Here a is the activity, p is the hydrostatic pressure, and $\bar{V}$ is the partial molar volume.

Introducing Eq. 6 into Eq. 5 gives the flux of the component i in the membrane:

$$J_i = -L_i (dRT \ln^m a_i + {}^m \bar{V}_i dp) \quad (7)$$

Since in the membrane the pressure is constant, i.e., $dp = 0$ and since $d \ln a = \frac{da}{a}$ Eq. 5 can be written as:

$$J_i = -L_i RT \frac{d^m a_i}{{}^m a_i} \quad (8)$$

Integration of Eq. 8 across the membrane gives the flux as function of the activity of the component i in the membrane at the interface between the feed gas and the permeate gas:

$$J_i = -L_i \frac{RT}{{}^m \bar{a}_i} \frac{{}^m a_i^p - {}^m a_i^f}{\Delta z} \quad (9)$$

Here ${}^m \bar{a}_i$ is the average activity of the component i in the membrane, and the superscripts f and p refer to product side and feed side of the membrane.

Since at the interface between the membrane and the gas the chemical potentials of the component i in the membrane and the gas are equal, i.e.,

${}^m \mu_i = {}^g \mu_i$, the activity of the component i in the membrane at the interface can be expressed by its activity in the gas.

The chemical potential of the component i in the membrane and in the gas is obtained by integration of Eq. 6.

In the membrane the partial molar volume of the component can be considered as constant and equal to the molar volume of the condensed gas.

Thus is:

$${}^m \mu_i = \mu_i^o + RT \ln^m a_g + {}^m \bar{V}_i ({}^m p - p^o) \quad (10)$$

Here the superscript o refers to a standard state.

In the gas the partial molar volume is a function of the pressure and in accordance with the ideal gas law $\bar{V}_i$ must be replaced by $\frac{RT}{p}$.

The chemical potential in the gas is then given by:

$${}^g \mu_i = \mu_i^o + RT \ln^g a_g + RT \ln \frac{p}{p_i^o} = \mu_i^o + RT \ln \frac{{}^g a_i p}{p_i^o} \quad (11)$$

Since the chemical potentials in the membrane and the gas at the gas membrane interface are equal it is:

$$\begin{aligned} {}^g \mu_i = {}^m \mu_i &= RT \ln \frac{{}^g a_i p}{p_i^o} = RT \ln^m a_i + {}^m \bar{V}_i ({}^m p - p^o) \\ &= \frac{{}^g a_i p}{p_i^o} = {}^m a_i \exp \frac{{}^m \bar{V}_i ({}^m p - p^o)}{RT} \end{aligned} \quad (12)$$

Here p_i^o is the saturation pressure of the gas.

It can be shown that the exponential term in Eq. 12 even at high pressure is always close to 1. Therefore, the activity of the component i at the interface with the gas can be expressed by:

$${}^m a_i^f = \frac{{}^g a_i^f p^f}{p_i^o} \text{ and } {}^m a_i^p = \frac{{}^g a_i^p p^p}{p_i^o} \quad (13)$$

Here the superscripts f and p refer to feed and permeate side of the membrane.

The activity of the component i in the membrane and in the gas can be related to its concentration in the membrane and its molar fraction in the gas by:

$${}^m a_i = {}^m X_i {}^m \gamma_i \text{ and } {}^g a_i = \frac{X_i \varphi_i}{p_i^0} \quad (14)$$

Here X is the molar fraction, γ is the activity coefficient, φ is the fugacity coefficient, and the superscripts m , g , and o refer to the membrane, the gas phase, and the saturation pressure.

Introducing Eqs. 13 and 14 into Eq. 9 leads to:

$$J_i = -L_i \frac{RT}{m \bar{X}_i {}^m \bar{\gamma}_i p_i^0} \frac{X_i^p p^p \varphi_i^p - X_i^f p^f \varphi_i^f}{\Delta z} \quad (15)$$

Here L is a phenomenological coefficient, X is the molar fraction in the gas, p is the pressure, φ is the fugacity coefficient, and ${}^m \bar{X}_i$ and ${}^m \bar{\gamma}_i$ are the average molar fraction and the average activity coefficient of the component i in the membrane, Δz is the thickness of the membrane, and the superscripts p , f , and o refer to permeate, feed, and saturation pressure, the subscript i refers to a component.

Introducing the relation between the phenomenological coefficient and the diffusion coefficient, which is $L_i = \frac{D_i C_i}{RT}$, and the relation between the molar fraction and the concentration which is ${}^m C_i = X_i \frac{{}^m \rho}{M_i}$, and assuming to a first approximation that the fugacity coefficients in the feed and the permeate are the same, i.e., $\varphi_i^p = \varphi_i^f$ Eq. 15 becomes:

$$J_i = -D_i \frac{\varphi_i^m \rho}{m \bar{\gamma}_i p_i^0 M_i} \frac{X_i^p p^p - X_i^f p^f}{\Delta z} \quad (16)$$

Introducing a sorption coefficient which is given by: $k_i = \frac{\varphi_i^m \rho}{m \bar{\gamma}_i p_i^0 M_i}$ into Eq. 4 leads to:

$$J_i = -D_i k_i \frac{X_i^p p^p - X_i^f p^f}{\Delta z} \quad (17)$$

Here D is the diffusion coefficient in the membrane, k_i is the gas sorption coefficient of the

membrane, ρ is the density, and M is the molecular weight, and the subscript i refers to a component.

The product of diffusion and sorption coefficient is the membrane permeability given by $P_i = D_i k_i$. Introducing the permeability P_i into Eq. 17 gives the flux J_i of a component through the membrane as a function of its molar fractions in the feed and permeate X_i^f and X_i^p , its fugacity coefficient φ_i , its permeability in the membrane P_i , the membrane thickness Δz , and the pressures in the feed and permeate p^f and p^p .

$$J_i = -P_i \frac{X_i^p p^p - X_i^f p^f}{\Delta z} \quad (18)$$

In deriving Eq. 18 several assumptions have been made which are generally valid for permanent gases. However, the assumption that the diffusion and the solubility coefficient are independent of concentration and pressure is not valid for easily condensable vapors. In permeation of organic vapors, the diffusion coefficient may vary by several orders of magnitude with the concentration of the permeating component in the membrane.

For the relationship between the diffusion coefficient and the concentration of the diffusing component, different equations accounting for dual sorption or free volume and structural changes of the polymer are discussed in the literature. It should be pointed out that in gas and especially vapors permeation it is generally not possible to predict the mass transport behavior of various components in a mixture from single component measurements.

For a practical application the separation efficiency of the membrane is a crucial parameter. In gas permeation the separation efficiency of a membrane is expressed by its selectivity and/or its separation factor. The selectivity of a membrane for various components of a mixture is defined by the ratio of the permeability. For a binary mixture with the components k and j , the selectivity is:

$$S_{j,k}^P = \frac{P_j}{P_k} \quad (19)$$

Here, $S_{j,k}^p$ is the permeation selectivity of a membrane for the components j and k , and P_j and P_k are their permeability.

The permeation selectivity can be split into two terms, i.e., the selectivity due to different diffusion coefficients of the components of the gas mixture or due to their solubility in the membrane:

$$S_{j,k}^p = S_{j,k}^D S_{j,k}^k \quad (20)$$

Here $S_{j,k}^D$ and $S_{j,k}^k$ are the diffusivity and solubility selectivity of a membrane for the components j and k .

The selectivity is a useful parameter to characterize a membrane. For the design of a membrane plant, however, the separation factor is more useful. For a binary mixture the separation factor is defined by:

$$\alpha_{j,k} = \frac{X_j^p X_k^f}{X_j^f X_k^p} \quad (21)$$

Here α is the separation factor and X is the mole fraction, the subscripts k and j refer to the two components, and the superscripts f and p refer to the feed and the permeate.

The separation factor is defined to be always >1 . It is related to the membrane selectivity by:

$$\alpha_{j,k} = S_{j,k} \frac{\frac{X_j^p P^p}{P^f} - X_j^f}{\frac{X_k^p P^p}{P^f} - X_k^f} \frac{X_k^f}{X_j^f} \quad (22)$$

Here S is the selectivity for a binary mixture, p is the pressure, X is the molar fraction, and the superscripts f and p refer to the feed and the permeate, and the subscripts k and j refer to the components in the mixture. The separation factor is always smaller than the selectivity and when the pressure ratio of feed to permeate becomes infinitely high. Thus is:

$$\lim_{\frac{p^p}{p^f} \rightarrow 0} \alpha_{j,k} = S_{j,k} \quad (23)$$

In vapor separation α is normally a function of the feed concentration.

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Principle of Membrane Contactors

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Membrane contactors are systems where porous membranes are used to carry out mass transfer between phases. In membrane contactors the membrane does not work as a selective barrier, and it does not control the transport between the two adjacent phases. It is used as a nonselective interface placed between two phases where its function is to keep the two phases separated and in contact at the same time.

The key factor of the process is the use of porous membranes ($2 \cdot 10^{-3}$ – $1 \mu\text{m}$ of pore size) with different surface tension with respect to the phase to be separated. For example,

microfiltration membranes interposed between polar fluid (liquid or gas) phases. The membrane pores are sufficiently small to ensure that capillary and interfacial forces prevent direct mixing of the phases (as long as a transmembrane pressure value lower than the breakthrough pressure is used). In addition, porous membranes provide a large contacting surface area between the two phases.

Membrane contactors can be used to separate two immiscible liquids (liquid/liquid contactors, e.g., membrane-based solvent extraction or pertraction) as well as two miscible liquids. In this last case, a vapor phase is allowed to pass through the membrane pores under a temperature gradient, and the process is usually known as "membrane distillation." Membrane contactors are also used to absorb a component from a gas mixture into a liquid (gas/liquid contactor) or to remove dissolved gases from liquids (liquid/gas contactors). For membrane contactors that separate a gas and a liquid phase, it is of crucial importance that the phases also do not mix and therefore it is necessary that the liquid does not enter the pores. The transmembrane pressure, pore size, surface tension between liquid and membrane interface controls this. The relationship between pressure and pore size is described by Laplace equation:

$$\Delta P = -\frac{2\gamma \cdot \cos \vartheta}{r} \quad (1)$$

The liquid will not wet the membrane pore if the contact angle is greater than 90° . Supercritical fluid contactors aim to achieve transfer of species from a liquid phase into a supercritical carbon dioxide or vice versa.

Membrane Contactors Used to Separate Two Liquid Immiscible Phases

These types of contactors are used in membrane-based solvent extraction operations and in general the transport occurs between an aqueous and an organic phase. One of the two immiscible phases wets the membrane and contacts the other phase at

the pore mouth on the opposite side of the membrane. A higher transmembrane pressure from the nonwetting phase side keeps the wetting phase within the membrane pores avoiding its dispersion into the other phase. Based on the type of membrane, wetting phase, and transport direction, the following cases can be distinguished:

- The membrane is hydrophobic, the organic phase wets the membrane and the transport occurs from the aqueous to the organic phase.
- The membrane is hydrophobic, the organic phase wets the membrane and the transport occurs from the organic to the aqueous phase.
- The membrane is hydrophilic, the aqueous phase wets the membrane and the transport occurs from the aqueous to the organic phase.
- The membrane is hydrophilic, the aqueous phase wets the membrane and the transport occurs from the organic to the aqueous phase.

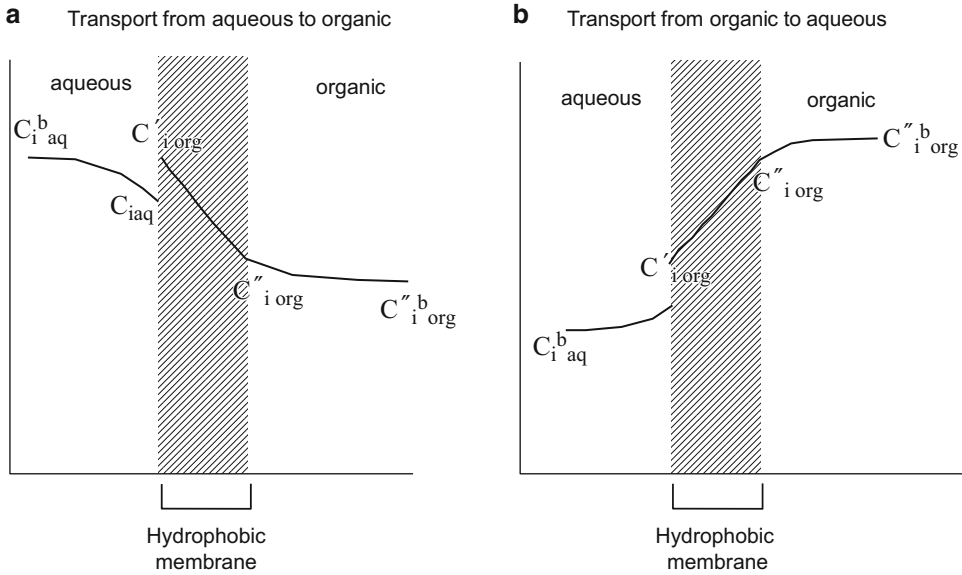
The theory of mass transfer in different systems has been reported by several authors (Prasad and Sirkar 1992). Figure 1a shows the solute concentration profile in hydrophobic flat membranes with organic in the side A and water in the side B. The organic phase wets the membrane and the extraction is from aqueous to organic.

The mass transport can be described in terms of resistances in series. In membrane contactor, the overall resistance to mass transport is given by three resistances: aqueous phase/membrane/organic phase:

$$\frac{1}{K_{tot}} = \frac{1}{k_{aq}} + \frac{1}{k_{pore}} + \frac{1}{k_{org}} \quad (2)$$

where, K_{tot} is the overall mass transfer coefficient; k_{aq} , k_{pore} , and k_{org} are the mass transfer coefficients in the aqueous phase, in the membrane pore, and in the organic phase, respectively.

For the various cases, assumptions can be made for negligible resistances respect to others. If bulk and surface transport resistance are considered negligible, transport occurs by diffusion under a concentration gradient. The solute flux from the aqueous to the organic phase bulk can be described by the general expression:



Principle of Membrane Contactors, Fig. 1 Solute concentration profile in hydrophobic flat membranes. (a) transport from aqueous to organic phase; (b) transport from organic to aqueous phase

$$J_i = k_{iaq} (C_{iaq}^b - C_{iaq}^o) = k_{imo} (C_{iorg}^o - C_{iorg}^{ob}) \\ = k_{iorg} (C_{iorg}^{ob} - C_{iorg}^{ob}) \quad (3)$$

Considering the organic side:

$$J_i = K_o (C_{iorg}^* - C_{iorg}^{ob}) \quad (4)$$

where, K_o is the overall mass transfer coefficient, C_{iorg}^* is an hypothetical organic phase concentration of component “i” in equilibrium with the bulk aqueous phase concentration (C_{iaq}^{ob}); C_{iorg}^{ob} is the concentration of component I in the organic bulk phase. These two concentrations are also related by a solute distribution coefficient:

$$m_i = \frac{C_{iorg}^*}{C_{iaq}^b} = \frac{C_{iorg}^o}{C_{iaq}^o} = \frac{C_{iorg}^{ob}}{C_{iaq}^{ob}} \quad (5)$$

where, C_{iaq}^* is an hypothetical aqueous phase concentration in equilibrium with the bulk organic phase concentration.

From these equations, a relation between K_o and the individual mass transfer coefficients is obtained:

$$\frac{1}{K_o} = \frac{m_i}{k_{iaq}} + \frac{1}{k_{imorg}} + \frac{1}{k_{iorg}} \quad (6)$$

From the aqueous side:

$$J_i = K_{aq} (C_{iaq}^b - C_{iaq}^*) \quad (7)$$

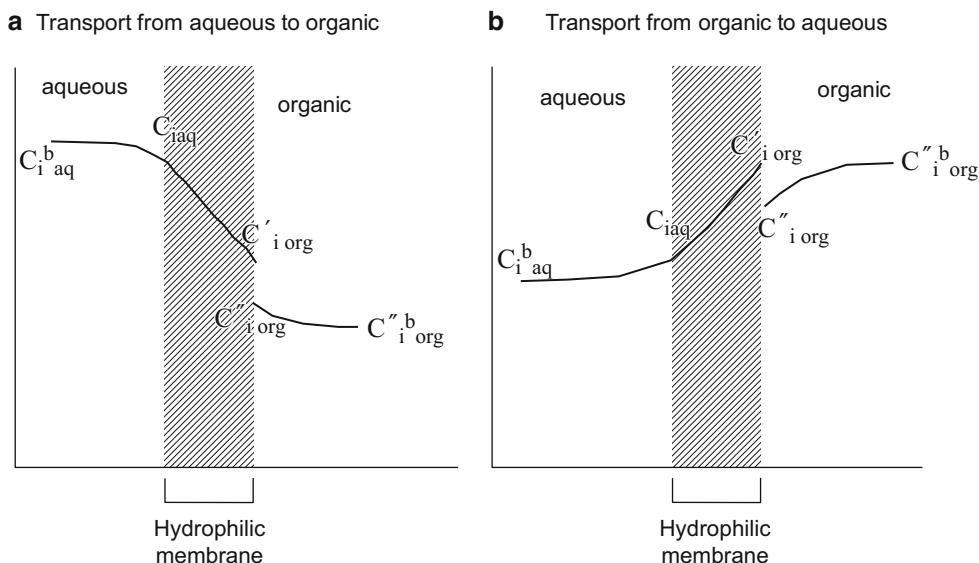
and

$$\frac{1}{K_{aq}} = \frac{1}{k_{iaq}} + \frac{1}{m_i k_{imo}} + \frac{1}{m_i k_{iorg}} \quad (8)$$

The profile concentration for transport occurring from the organic to the aqueous phase through a hydrophobic flat membrane is reported in Fig. 1b and relative equations are modified according to the direction of transport.

The cases of hydrophilic membranes wetted by aqueous phase are reported in Fig. 2a, b.

In these operations one of the phases involved is always a liquid, whereas the other one can be liquid or gaseous. The processes that can be performed are gas absorption, liquid scrubbing, and liquid-liquid extraction. They can be then considered as alternative systems to conventional packed towers and extractors. In all cases, the difference of concentration promotes the mass



Principle of Membrane Contactors, Fig. 2 Solute concentration profile in hydrophilic flat membranes. (a) transport from aqueous to organic; (b) transport from organic to aqueous phase

transport. In gas absorption and liquid scrubbing, the second phase is a gas from/to which volatile species are transferred. The membrane used is usually hydrophobic: the liquid phase is blocked at the pore entrance and the pores are gas filled; this configuration reduces the mass resistance given by the membrane due the volatile nature of the species that move from one phase to the other (their diffusion in gas is higher than in liquid). When compared to the resistance at the liquid side, the membrane is in fact usually negligible.

In liquid-liquid extraction, the phases involved are aqueous and organic (nonmiscible) and the membrane, as discussed before, can be hydrophobic or hydrophilic. The choice is always related to the situation that minimizes the mass resistance: usually, the phase in which the solute has higher solubility fills the membrane pores.

Membrane Contactors Used to Separate Two Miscible Liquids: Membrane Distillation

In this configuration system, a porous hydrophobic membrane is in contact with aqueous solutions

having different temperature on the two sides of the membrane.

The high interfacial tension between the hydrophobic membrane surface and the aqueous phase prevents the mass transfer of the aqueous phase as a liquid phase and forms a vapor-liquid interface at the pore entrance. Then the volatile compounds evaporate and are transported by diffusion and/or convection through the pores to the other side of the membrane where they are condensed and removed into the aqueous phase at lower temperature.

When the permeable side (often pure water) is in direct contact with the membrane, the system is known as direct contact membrane distillation (DCMD). There are also cases where the condensing phase is separated by an air gap from the membrane (AGMD), vacuum (VMD) or a sweep gas is used (SGMD).

Considering the mass transport in membrane distillation, the electrical potential can be neglected as neutral membranes and solvents are used, therefore the transport occurs under a chemical potential:

$$\Delta\mu = \bar{V}_i \Delta p + RT \ln \frac{a_i''}{a_i'} \quad (9)$$

Where, $\bar{V}_i$ is the partial molar volume of a component i ; a_i is the activity, and Δp is the hydrostatic pressure gradient.

In membrane distillation, the hydrostatic pressure gradient across the membrane is negligible. The driving force of the process is the vapor pressure difference across the membrane. The vapor liquid equilibrium for nonideal mixtures is described by:

$$p_i = Py_i = p_i^0 a_i = p_i^0 \gamma_i x_i \quad (10)$$

where, p is the total pressure, x_i and y_i are the liquid and vapor mole fraction, respectively.

Mass transfer for membrane distillation can be described in terms of resistances in series upon transfer between the bulks of two phases contacting the membrane. The surface boundary layer resistances are generally negligible. The controlling step is represented by the diffusion across the membrane.

In a porous medium, if surface diffusion is assumed negligible, mass transfer can be affected by viscous resistance (resulting from the momentum transferred to the supported membrane), Knudsen diffusion resistance (due to collisions between diffusing molecules), or ordinary diffusion (due to collisions between molecules and membrane walls) (Drioli et al. 2000n). Predominance, coexistence, or transition between all of these different mechanisms is estimated by comparing the mean free path λ of diffusing molecules to the mean pore size of the membrane (Knudsen number). Kinetic theory of ideal gases calculates λ as:

$$\lambda = \frac{k_B T}{P \sqrt{2} \pi \sigma^2} \quad (11)$$

where, k_B is the Boltzmann constant ($1.380 \cdot 10^{-23} \text{ JK}^{-1}$), and σ is the collision diameter of the molecule ($\sigma = 2.7 \text{ \AA}$ for water).

For the binary mixture of water vapor in air, the free mean path $\lambda_{a/w}$ can be evaluated at the average membrane temperature $\bar{T}$, by

$$\lambda_{a/w} = \frac{k_B \bar{T}}{\pi \left(\frac{\sigma_w + \sigma_a}{2} \right)^2} \frac{1}{P \sqrt{1 + \left(\frac{m_w}{m_a} \right)}} \quad (12)$$

where, P is the total pressure, σ_a ($=3.7 \text{ \AA}$) and σ_w the collision diameters, and m_a and m_w the molecular weight for air and water, respectively.

In the continuum region, the free mean path of the gas is small if compared with the average membrane pore diameter, and molecule-molecule collisions predominate over molecule-wall collisions. Knudsen number, defined as the ratio of the free path of the gas to the pore diameter, is < 1 and the flux can be described by the Darcy's law. In the Knudsen region this situation is reversed: the mean free path of the gas is large with respect to the average membrane pore diameter ($Kn > 1$), molecule-wall collisions predominate over molecule-molecule collisions, and the mass transport can be described by Knudsen's law. In many practical cases, λ is comparable to the typical pore size of membranes used in membrane distillation and no simplifications can be made in modeling the mass transfer operation. Dusty gas model (DGM) is frequently used for describing gaseous molar fluxes through porous media; the most general form (neglecting surface diffusion) is expressed as:

$$\frac{J_i^D}{D_{ie}^k} + \sum_{j=i \neq i}^n \frac{p_j J_i^D - p_i J_j^D}{D_{ije}^0} = -\frac{1}{RT} \nabla p_i \quad (13)$$

$$J_i^v = -\frac{\varepsilon r^2 p_i}{8RT \tau \eta} \nabla P \quad (14)$$

$$D_{ie}^k = \frac{2\varepsilon r}{3\tau} \sqrt{\frac{8RT}{\pi M_i}} \quad (15)$$

$$D_{ije}^0 = \frac{\varepsilon}{\tau} P D_{ij}^0 \quad (16)$$

where, J^D is the diffusive flux, J^v the viscous flux, D^k the Knudsen diffusion coefficient, D^0 the ordinary diffusion coefficient, p the partial pressure, R the gas constant, T the temperature, P the total pressure, η the gas viscosity, r the membrane radius, ε the membrane porosity, and τ the membrane tortuosity. Subscript e indicates the "effective" diffusion coefficient, calculated by taking into account the structural parameters of the membrane as shown in Eqs. 13 and 14.

Although dusty gas model was derived for isothermal systems, it is successfully applied in membrane distillation working under relatively small thermal gradients by assuming an average value of temperature across the membrane.

The adoption of empirical correlations is in some cases preferred. The transmembrane flux can be written as a linear function of the vapor pressure difference across the membrane:

$$J = C\Delta p \quad (17)$$

where, C is the membrane distillation coefficient, and Δp the partial pressure gradient evaluated at the membrane surfaces. In Eq. 14, the membrane distillation coefficient C is a function of the membrane properties (pore size, thickness, porosity, and tortuosity), properties of the vapor transported across the membrane (molecular weight and diffusivity), and operative temperatures.

At steady state, the heat flux can be written as:

$$Q = H\tau(T_h - T_c) \quad (18)$$

Where, Q is the heat flux; T_h and T_c are the temperature of the hot and cold side, respectively; H is the membrane heat transfer coefficient; τ is the temperature polarization coefficient.

The temperature polarization coefficient is defined as:

$$\tau = \left(\frac{T_1 - T_0}{T_h - T_c} \right) \quad (19)$$

where, T_1 and T_0 are the temperatures at the membrane interface.

As an indirect contact membrane distillation, in osmotic distillation the two phases involved are always aqueous solutions and the membrane hydrophobic; the principle of transport through the membrane pores is also the same as in membrane distillation. The only difference is related to the driving force used to promote the evaporation flux that is now achieved by using at the distillate side a hypertonic salt solution: the difference in solute concentrations between the solution to be treated and the distillate side leads to a vapor pressure difference which causes the transport of

the water vapor molecules. This different way of carrying out the process allows to operate at ambient temperature, without the need to heat the solution to be concentrated, and can be very useful when is important to avoid any phenomenon of denaturation of the solution. Also in this case, the resistance offered by the membrane is negligible. The resistances at the liquid sides lead now to a profile of concentration (concentration polarization) that affects the driving force and reduces the performance of the system. A control and optimization of the fluid-dynamic allows to minimize this phenomenon. The transmembrane flux can be calculated by:

$$C_m = C_b \exp\left(-\frac{J}{k}\right) \quad (20)$$

Where, k is the solute transfer coefficient in the liquid phase, C_b and C_m are the concentration in the bulk and at the membrane level, respectively.

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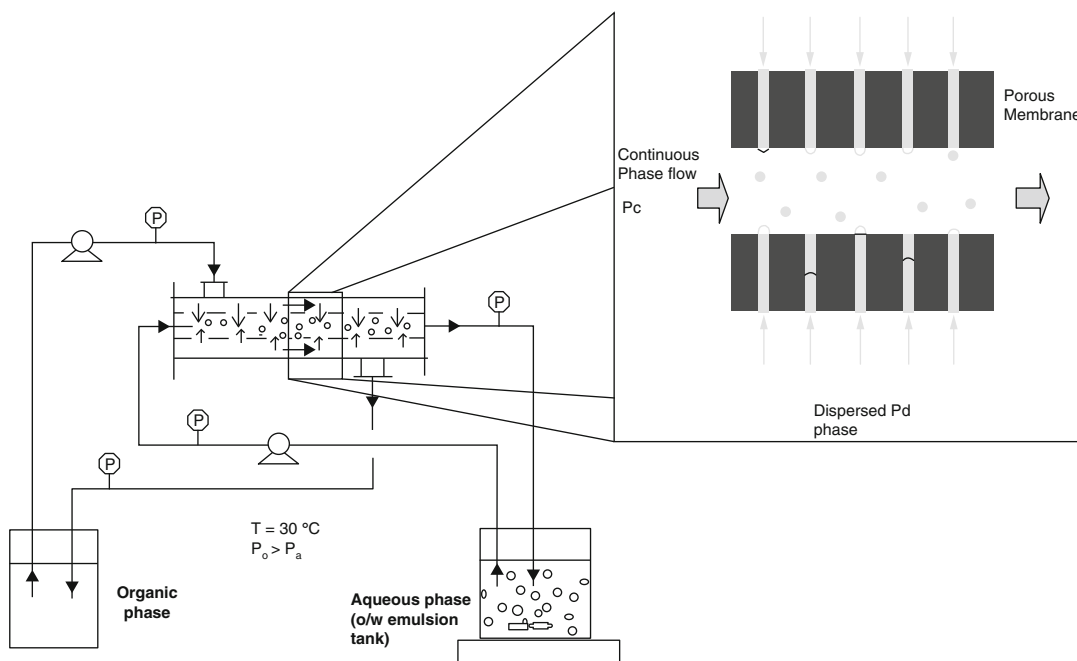
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Principle of Membrane Emulsifier

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Membrane emulsifier is used to prepare oil-in-water, water-in-oil, water-in-oil-in-water, etc. emulsions. In this type of system, the porous



Principle of Membrane Emulsifier, Fig. 1 Schematic of a membrane emulsifier apparatus

membrane is used to disperse, drop by drop, an immiscible phase (named disperse phase) into another phase (named continuous phase). The disperse phase is present as small droplets suspended in the continuous phase.

In membrane emulsification, droplets are formed at the pore mouth of a membrane by forcing the dispersed phase to permeate through the membrane and stripping the droplets from the pore into the continuous phase by action of the axial velocity, Fig. 1. The driving force is a difference of pressure between the two phases. An important aspect is that the membrane is not wetted by the dispersed phase and the choice of the membrane strongly depends on this fact. Therefore, to prepare oil-in-water emulsion a hydrophilic membrane is used, as the oil phase does not wet the hydrophilic membrane. Both liquid streams and the membrane itself offer the resistance to the mass transport.

The droplet size depends on the balance between (i) properties of components (viscosity, interfacial tension, densities); (ii) properties of membrane (pore size and shape, porosity, wall

contact angle, tortuosity); and (iii) process parameters (transmembrane pressure, pressure drop, permeate flow of dispersed phase, axial velocity (drug force) of continuous phase, temperature) (Schroder et al. 1998).

Stability and density of emulsions prepared by membranes are very good, but productivity might represent a limiting aspect for large-scale application. In other words, low permeation rate is in general associated with emulsions having narrow size and uniform distribution.

The theoretical description of a membrane emulsification mainly takes into account the permeation of the dispersion phase through the membrane pores and the detachment mechanism of the droplet (Williams et al. 1998; Josceline and Tragardh 2000; Abrahamse et al. 2001; De Luca et al. 2004).

The flux of the disperse phase through the porous membrane may be assumed to occur by convection and to follow Darcy's Law when considering pores of cylindrical geometry. The equation reduces to the Hagen-Poiseuille equation. In the case of one active pore, the dispersed flow rate can be obtained as

$$Q_d = \frac{\pi d_p^4}{128 \xi} \frac{\Delta P_{\text{eff}}}{\mu_d L} \quad (1)$$

where Q_d is the flow rate of the dispersed phase; d_p is the pore diameter; μ_d is the viscosity of the dispersed phase; ξ is the pore tortuosity; L is the membrane thickness.

The transmembrane pressure is defined as the difference of applied pressures between each side of the membrane and it consists of two parts: capillary pressure, ΔP_γ , due to the curvature of the interface and to the dynamic interfacial tension, and the effective transmembrane pressure

$$\Delta P_{\text{eff}} = \Delta P_{tm} - \Delta P[\gamma(t), d_d] \quad (2)$$

or the drag of the disperse phase inside the pore which determines Q_d .

The droplet at the pore tends to form a spherical shape, whose radius of curvature, $d_d/2$, is related to the height of the spherical droplet, h , and to the membrane pore radius $d_p/2$ by

$$\frac{d_d}{2} = \frac{(d_p/2)^2 + h^2}{2h} \quad (3)$$

When the height of the growing droplet equals the pore radius, the droplet size reaches its minimum, $d_d = d_p$. Accordingly, the capillary pressure calculated by Laplace equation takes a critical value offering the maximum resistance to the disperse phase flow.

Droplet formation at an individual pore involves droplet growth and droplet detachment (Schroder et al. 1998; Peng et al. 1998). The growth process ends when a balance among all mechanical torques acting on the droplet is reached. At the end of this stage the droplet is still connected to the pore through a neck. When the connection is interrupted the detachment is completed.

The main forces acting on a droplet to determine its growth and detachment have been identified and reported in the literature (Schroder et al. 1998; Peng et al. 1998; Wang et al. 2000):

$$F_D = k_x 3\pi \mu_c d_d v_c^\infty \approx \frac{3}{2} k_x \pi \tau_w d_d^2 \quad (4)$$

F_D is the drag force produced by the continuous phase flow; k_x the wall correction factor; v_c^∞ the undisturbed tangential velocity of the continuous phase at the droplet center; τ_w the wall shear stress. The relationships of the continuous phase velocity and τ_w are widely reported either for laminar or for turbulent flow (Wang et al. 2000).

The main forces that account in the droplet formation are

- The interfacial tension force,

$$F_\gamma = \pi d_p \gamma(t); \quad (5)$$

- The force due to the difference of pressure needed to overcome capillarity,

$$F_{sp} = \frac{\gamma(t)}{d_d} \pi d_p^2 \quad (6)$$

- The dynamic lift force,

$$F_{dl} = \frac{0.761 \tau_w^{1.5} \rho_c^{0.5}}{\mu_c} d_d^3 \quad (7)$$

Assuming that the shape of the droplet is approximately spherical, the droplet size can be estimated from the following equation:

$$F_D \frac{d_d}{2} = \left(\sum_i F_i \right) \frac{d_p}{2} \quad (8)$$

which provides a relationship between the membrane pore size and the droplet size at equilibrium.

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Principle of Membrane Reactors

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Membrane reactors are systems where a chemical or biochemical conversion is combined with a membrane operation.

The two main areas of membrane reactors are identified by the type of catalyst used, traditional chemical catalysts, or catalysts of biological origin, which also dictates the operating conditions. Hence, membrane reactors (mainly inorganic) working at high temperature ($100 < T < 600\text{ }^{\circ}\text{C}$) or membrane bioreactors working at low temperature ($<100\text{ }^{\circ}\text{C}$) are known (Giorno and Drioli 2010; Marcano and Tsotsis 2004).

In both types of reactors the membrane works in two main ways. In one case, the membrane is catalytically inert, it does not participate in the reaction directly, and it simply acts as a barrier to reaction components allowing selective supply of substrate and separation of the product(s) or intermediate(s). This type of system is known by the general term “membrane reactor.” In the other type of reactor, besides the ability to separate and compartmentalize, the membrane is also “catalytic,” the membrane itself is formed of catalytic moieties (e.g., zeolites, palladium, etc.), or it contains the (bio)catalyst (e.g., enzyme-loaded

membranes, TiO_2 , etc.); the membrane participates directly to the reaction. This type of system is called “catalytic membrane reactor.”

Membrane science and chemical and biochemical engineering contribute to the development of these systems by designing compact and flexible apparatuses where a chemical reaction is combined to a separation step in order to increase conversion. In fact, the separation process allows to remove product(s) from the reaction site thus enhancing the yield, according to Le Chatelier’s principle, by shifting the chemical equilibrium toward the formation of product.

Reaction yield and selectivity may strongly depend on membrane characteristics. This is true for reactions catalyzed by inorganic catalysts and in particular for reactions catalyzed by biocatalysts (e.g., enzymes, cells, etc.). In fact, in this case, in addition to the effects of membrane selectivity on reaction (e.g., by removing products or poisoning components) the physical-chemical properties of membranes may influence the catalyst structure (and therefore the catalyst selectivity) itself.

The use of polymeric membranes is more common for biocatalytic reactors as these systems can work in mild conditions of temperature and pressure. Due to the capabilities of membrane processes and biocatalysts to work with high selectivity, and of not requiring additives, biocatalytic membrane reactors are particularly promising for processes in the food and beverage, biotechnological, biomedical, and pharmaceutical fields.

The development of membranes made of various inorganic materials enlarged the application to a wider range of temperature and pressure conditions. Inorganic membranes are stable at higher temperature and have good chemical and mechanical resistance.

The type of reactions investigated in this area include dehydrogenation, esterification, hydrogenation, and partial and total oxidation.

Traditionally, the membrane reactors were applied in equilibrium-limited reactions. Nowadays, new applications are growing; for example, in biocatalytic reactors, the membrane can be used to remove some intermediate or side product that might deactivate the biocatalyst. In some cases, the membrane does not need to be selective, but it

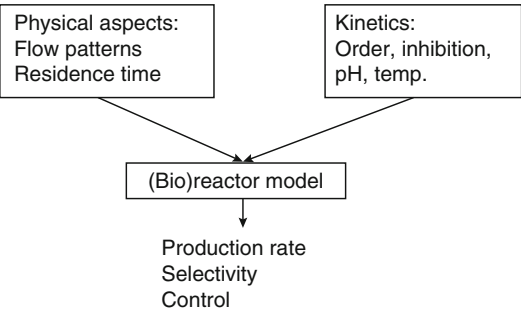
serves as a contacting reactive interface between the phases flowing on the two separate sides of the membrane.

The modeling of chemical and biochemical membrane reactors mainly depends on the function of the membrane; for example, if the membrane works as a separation unit independent from the reaction, then the reactor is modeled according to traditional systems (e.g., continuous stirred tank reactors, plug-flow reactor, etc.) combined to a membrane separation; if the membrane is catalytic, then the intrinsic kinetic and mass transport at the membrane level must be considered.

General concepts in reactor design can be applied to the membrane reactor too. In Fig. 1 is summarized the information needed for reactor development.

The building of models and their comparison with experimental data are useful and reasonable approaches to investigate and understand reactor performance.

Both kinetics and transport properties are needed.



Principle of Membrane Reactors, Fig. 1 Data needed for reactor design

The general procedure to formulate the mass balance is

- Choose the balance region so that the variables are constant or change little within the system and draw boundaries around the balance region.
- Identify the transport streams which flow across the system boundaries (e.g., convective in, convective out; diffusive in, diffusive out).
- Write the balance (e.g., rate of accumulation of mass of i = rate of i in by flow – rate of i out by flow + rate of production of i by reaction).
- Express each balance term by measurable variables in mathematical form. Pressure (P), volume (V), concentration (C), flow rate (F) are usually the measured variables (total mass = ρV ; mass of i = $C_i V$).
- Introduce other relationships and balances so that the number of equations equals the number of dependent variables.
- Express the total mass balance:

$$\frac{dVC}{dt} = (FC_i)_{\text{IN}} - (FC_i)_{\text{OUT}} + (r_i V)_{\text{system}} \quad (1)$$

The steady-state balance equation for a membrane reactor working in reaction-limited regime can be written as

$$FC_f - FC_p + v_r V = 0 \quad (2)$$

where C_f and C_p are the feed and permeate concentration, respectively, v_r the reaction rate, and V the reactor volume.

From this, the reaction rate can be derived:

Principle of Membrane Reactors, Table 1 Component balances for various tank reactor systems

Reactor type	Terms in equation	Final form
Batch reactor	Flow term = 0	Acc = Production
Fed batch or semi-cont. reactor	Flow term out = 0	Acc = In + Production
Steady state CSTR	Acc = 0	In – Out + Prod = 0
Component C_i does not react	Prod = 0	Acc = In – Out
Constant volume CSTR	Simplifies to $V(ds/dt) = F(S_0 - S_1) + r_s V$	Acc = In – Out + Prod

$$V_r = \frac{F(C_f - C_p)}{V} \quad (3)$$

Table 1 summarizes the component balances for various reactor systems.

The most relevant examples for biological and inorganic membrane reactor will be discussed in the following.

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Principle of Microfiltration

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Synonyms

Mass transfer in microfiltration

Principle of Microfiltration,
Fig. 1 Schematic drawing illustrating the principle of microfiltration

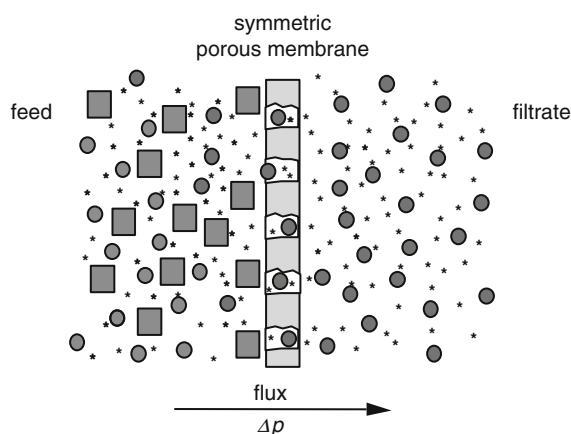
Microfiltration is a physical separation process that uses porous membranes with an average pore size between 0.1 and 10 μm . It promotes the separation of particles and dissolved components from fluids by a sieving mechanism, based on size exclusion. The principle of microfiltration is depicted in Fig. 1. The membrane separating a feed solution from a permeate or filtrate has a symmetric or asymmetric porous structure.

The driving force for the mass transport across the membrane is a pressure gradient. Since only large particles with diameters in excess of ca. 0.1 μm are separated by the membrane, the diffusion of particles and the osmotic pressure difference between the feed and filtrate solution are negligibly low, and the mass flux through a microfiltration membrane is given to a first approximation by:

$$J_v = \sum_i J_i \bar{V}_i \cong L_v \frac{\Delta p}{\Delta z} \quad (1)$$

Here J_v is the volume flux across the membrane, the subscripts v and i refer to volume and components in the solution, $\bar{V}$ is the partial molar volume, p is the pressure, L_v is a phenomenological coefficient referring to hydrodynamic permeability of the membrane, Δp is the pressure difference between the feed and filtrate solution, and Δz is the thickness of the membrane.

The mass transport in microfiltration membranes takes place by viscous flow through the



pores. The solid membrane matrix can be considered as completely impermeable. Therefore, the hydrodynamic permeability can be expressed in terms of the membrane pore size and the porosity and the solution viscosity according to Hagen-Poiseuille's law, which is given by:

$$J_v = \frac{\varepsilon r^2}{8\eta\tau} \frac{\Delta p}{\Delta z} \quad (2)$$

Here J_v is the flux, ε is the membrane porosity, r is the pore radius, η is the viscosity, τ is the tortuosity factor, Δp is the pressure difference across the membrane, and Δz is the membrane thickness.

The porosity is defined as the ratio of the pores' surface area to the membrane surface area. The porosity is always $\varepsilon < 1$. The tortuosity factor is defined as the ratio of the actual pore length to the thickness of the membrane taking into account that the pore length in general is somewhat longer than the cross section of the membrane. Thus, it is always $\tau > 1$.

Pressure difference between feed and permeate (i.e., transmembrane pressure) in the range of 0.1 and 2 bar is usually applied. Permeability value $>1,000 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$ is usually obtained with microfiltration membranes.

Another parameter which is of interest for the practical application of microfiltration is the separation characteristic of a membrane, which is generally expressed by the retention or rejection and is given by:

$$R_i = \left(1 - \frac{C_i^p}{C_i^f} \right) \quad (3)$$

Here R is the rejection coefficient, C is the concentration, the subscript i refers to a given component in the feed and the permeate, and the superscripts f and p refer to the feed and permeate or filtrate solutions. R is always ≤ 1 and a function of the particle and the pore size and pore size distribution. $R = 0$ means complete permeation, and $R = 1$ means complete rejection.

To account for changes in retentate concentration with increasing of volume reduction factor

(when operating in concentration mode) or with increasing of treated volume (when operating at constant volume) as well as for changes in membrane properties due to fouling as a function of time, the rejection is also evaluated on the basis of concentration of retentate (C_i^R) instead of the initial feed solution:

$$R_i = \left(1 - \frac{C_i^p}{C_i^R} \right) \quad (4)$$

Compared with conventional concentration processes, microfiltration appears to be a good alternative for minimizing the adverse effects of heat. In general, filtration processes do not involve phase changes or high temperatures, thus favoring the maintenance of the sensory and nutritional characteristics of the product.

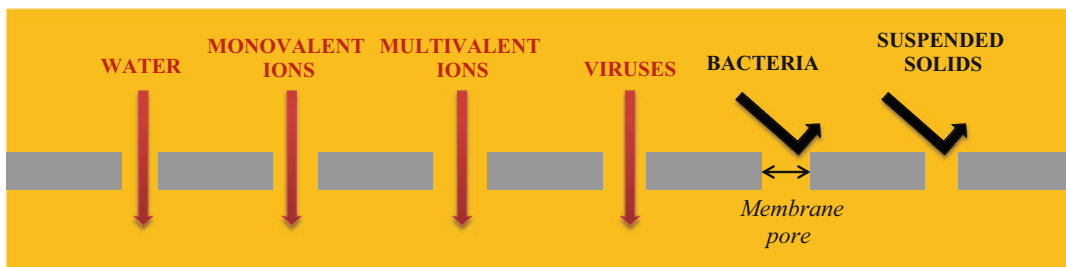
Microfiltration is used in a wide variety of industrial applications where particles of size $>0.1 \mu\text{m}$ have to be retained from the liquid (such as bacteria and suspended solid) (Fig. 2). The main industrial applications are cold sterilization of beverages and pharmaceutical products, clarification of fruit juice, wine, and beer, and wastewater treatment (Mulder 1996).

The materials which constitute the membranes used in microfiltration systems may be either organic (polymeric materials) or inorganic (ceramic, glassy, and metallic materials), depending upon the contaminants that are desired to be removed or the type of application. Module configurations include hollow fiber, tubular, flat sheet, spiral wound, rotating, and vibrating devices.

A basic microfiltration set-up comprises a feed tank, a pump to force liquid through the membrane, and two pressure gauges mounted before and after the membrane to read the corresponding hydrodynamic pressure drop across the membrane. Microfiltration membranes can generally operate in one of two configurations (Scott and Hughes 1996):

Cross-flow filtration (Fig. 3a): the feed streams flow tangential to a membrane surface, and as

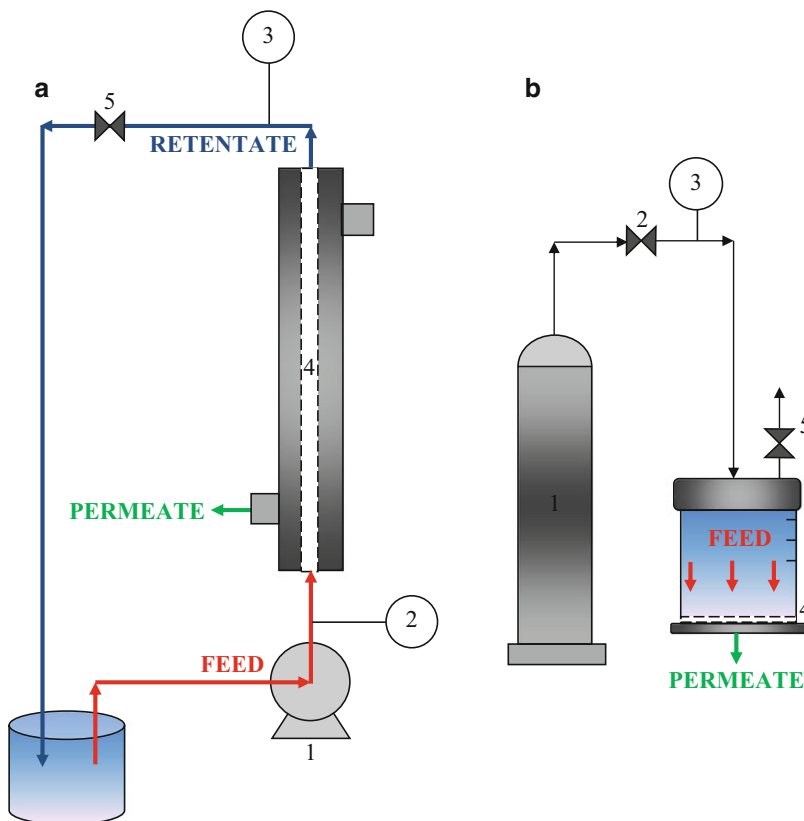
MICROFILTRATION PROCESS



Principle of Microfiltration, Fig. 2 Microfiltration process characteristics

Principle of Microfiltration,

Fig. 3 Scheme of microfiltration membrane set-up. (a) Cross-flow configuration: 1 pump, 2 and 3 pressure gauges, 4 tubular membrane, 5 back-pressure valve; (b) dead-end configuration: 1 nitrogen gas vessel, 2 back-pressure valve, 3 pressure gauge, 4 flat sheet membrane, 5 purge valve



a result of the application of an appropriate driving force, a permeating species passes through the membrane. Solution that is directed to the membrane surface is called the feed. Solution that passes along the membrane surface and back to the feed reservoir is the retentate. This solution is usually pumped back to the feed reservoir and recirculated.

Solution that passes the membrane is the permeate.

Dead-end filtration (Fig. 3b): all the feed flows perpendicular to the membrane surface, and the retained particles accumulate on the surface forming a filter cake. The thickness of this cake therefore increases with time and is either cleaned or replaced.

Principle of Microfiltration, Table 1 Comparison of advantages and disadvantages of cross-flow and dead-end microfiltration

Dead-end filtration	Cross-flow filtration
Low capital cost	High capital cost
High operating costs – membrane must be replaced after each use, and disposal can be a problem	Modest operating costs – membranes have extended lifetimes if regularly cleaned
Operation is simple – no moving parts	Operation is complex – filters require regular cleaning
Best suited to dilute (low solid content) solutions. Membrane replacement costs increase with particle concentrations in the feed solution	Best suited to high solid content solutions. Costs are relatively independent of feed solution particle concentrations

The most important properties of cross-flow and dead-end microfiltration are summarized in Table 1 (Baker 2004).

During the membrane filtration process, permeate flux may decrease significantly and rapidly until a final steady state as a consequence of fouling and concentration polarization phenomena.

The approaches to minimize the effects of membrane fouling and concentration polarization include (Hilal et al. 2005):

Feed pretreatment by using physical and chemical processes: the physical process usually consists of prefiltration to remove any suspended particles that may plug the module or adhere to the surface membrane. Chemical process involves addition of flocculation-coagulation agents limiting the membrane fouling by aggregation of the colloid fraction.

Membrane modification by using coating and grafting techniques in order to minimize and/or eliminate adhesive fouling.

Optimization of operating parameters: flow manipulation is the main focus of changing the operating parameters by using different strategies such as inserts, turbulence promoters, increased flow rates, mixers, backflushing, backpulsing, backwashing, and air sparging.

Cleaning procedures: the method involves the use of cleaning agents (such as acids, bases, enzymes, surfactants, and disinfectants) able to affect fouling material present on a membrane surface by removing or changing the morphology of the foulants or altering the surface chemistry properties of the deposit.

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Principle of Nanofiltration (NF)

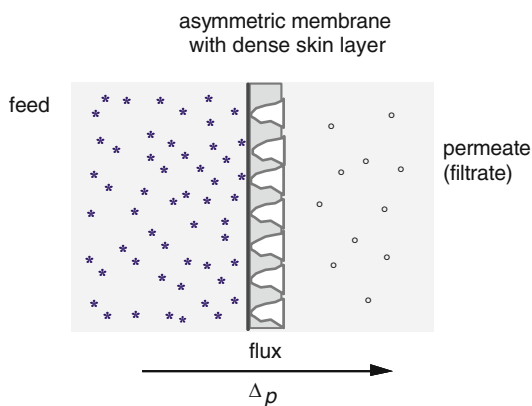
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Synonyms

Mass transfer in NF

Nanofiltration (NF) is very similar to ultrafiltration and to reverse osmosis. In all three processes,

a hydrostatic pressure is applied to transport a molecular mixture to the surface of a membrane. In general, the solvent and some low molecular weight solutes permeate the membrane while other components are retained. The main difference between nanofiltration and ultrafiltration is the pore size of the membrane and thus the molecular weight of the components that are retained by the membrane. Ultrafiltration membranes have pores with diameters in the range of 2–10 nm, and components are separated by a sieving mechanism according to their size. The molecular weight cut-off of ultrafiltration membranes is between 1000 and 10^6 Da. Nanofiltration membranes have pore sizes between 0.5 and 2 nm, which correspond to a molecular weight cut-off value of about 400–500 Da. Due to the smaller pores, the permeability of nanofiltration membranes is lower than that of ultrafiltration membranes. Furthermore, the osmotic pressure of the solutions treated by nanofiltration may have a significant osmotic pressure. Therefore, the applied pressure is in general about an order of magnitude higher than in ultrafiltration but lower than in reverse osmosis. The main difference between nanofiltration and reverse osmosis is the transport mode in the membrane. While in nanofiltration, it is assumed that all components permeate the membrane exclusively through geometrically well-defined pores; it is assumed that in reverse osmosis the different components permeate the membrane by diffusion through a more or less homogeneous polymer matrix, and the separation is due to the solubility and the diffusivity in the polymer matrix. But there is an additional difference between ultrafiltration or reverse osmosis membranes. While both ultrafiltration and reverse osmosis are neutral, nanofiltration membranes carry often positive or negative electrical charges. Therefore, the separation properties of nanofiltration membrane are determined in general by two distinct properties: (1) the pore size of the membranes, which corresponds to a molecular weight cut-off value of about 400 (± 100) Da and (2) the surface charge which can be positive or negative and affects the permeability of charged components such as salt ions. Due to the electric interactions between ions and the membrane



Principle of Nanofiltration (NF), Fig. 1 Schematic drawing illustrating the principle and the mass transport in nanofiltration (Strathmann et al. 2006)

surface charge, for example, nanofiltration membranes are capable of separating monovalent from multivalent ions.

A schematic illustration of the principle of nanofiltration is shown in Fig. 1.

To describe the mass transport in nanofiltration as function of a hydrostatic pressure driving force, the same basic relations as used in ultrafiltration can be applied.

The transport of the individual can be described by:

$$J_i = L_i \frac{d\mu_i}{dz} = L_i \frac{d}{dz} (\bar{V}_i p + RT \ln a_i) + L_v^m C_i \frac{dp}{dz} \quad (1)$$

The total volume flux through the membrane is given by sum of the molar flux of the individual components multiplied by their molar volume:

$$J_v = \sum_i J_i \bar{V}_i = \sum_i \bar{V}_i L_i \frac{d}{dz} (\bar{V}_i p + RT \ln^m a_i) + L_v \frac{dp}{dz} \quad (2)$$

Here, J_v is the total volume flux and J_i that of the individual components, L_i is a phenomenological coefficient referring to the diffusion of the permeating components within the membrane pores, L_v is the hydraulic permeability of the membrane,

referring to the viscous flow through the pores, $\bar{V}$ is the partial molar volume, and μ_i the chemical potential of a component i , p is the hydrostatic pressure, and z is a directional coordinate.

The first term in Eqs. 1 and 2 describes the diffusive fluxes of the different components in the pores of the membrane under the driving force of a chemical potential gradient, and the second term describes the viscous flow of the solution through the pore due to the applied pressure.

Expressing the phenomenological coefficient L_w by $L_w = \frac{D_w C_w}{RT}$ and integration of Eq. 2 over the pore length and expressing the water activity gradient in the pores by the osmotic pressure difference between the feed and the filtrate lead to:

$$\begin{aligned} J_v &\cong \frac{\bar{V}_w^2 L_w}{\Delta z} (\Delta p + \Delta \pi) + L_v \frac{\Delta p}{\Delta z} \\ &= \left(\frac{D_w \bar{V}_w}{RT} + L_v \right) \frac{\Delta p}{\Delta z} + \frac{D_w \bar{V}_w}{RT} \frac{\Delta \pi}{\Delta z} \end{aligned} \quad (3)$$

Here, $\Delta \pi$ and Δp are the osmotic and the hydrostatic pressure differences between the feed solution and permeate.

It can easily be shown that for nanofiltration membranes with pore sizes in the range of ca. 1 nm the term $\frac{D_w \bar{V}_w}{RT}$ is of the same order of magnitude or large than the L_v . Thus, unlike in ultrafiltration the effect of the osmotic pressure on the solvent flux cannot be neglected in nanofiltration. Therefore, solvent flux at a given hydrostatic pressure difference is a function of the feed and permeate concentration.

If it is assumed that the solutions treated in nanofiltration are relatively dilute and that to a first approximation the activities of the individual components can be replaced by their concentrations. Equation 1 can be expressed by:

$$\begin{aligned} J_i &= {}^m D_i \frac{d}{dz} \left(\frac{\bar{V}_i {}^m C_i}{RT} dp + d {}^m C_i \right) \\ &\quad + L_v {}^m C_i \frac{dp}{dz} \end{aligned} \quad (4)$$

Here, the phenomenological coefficient is expressed by the diffusion coefficient, i.e., ${}^m D_i = L_i \frac{RT}{{}^m C_i}$.

In ultrafiltration, the concentration of a dissolved component in the membrane is related to that in the feed and permeates by a partition coefficient. The same is true in nanofiltration. The concentration in the membrane is:

$${}^m C_i = k_i {}^s C_i \quad (5)$$

Here, k_i is the partition coefficient, ${}^m C_i$ and ${}^s C_i$ are the concentrations of a component in the membrane and in the solution, respectively.

However, if the membrane carries positive or negative electric charges at the surface, the partition coefficient for ionic components such as salt ions is not only determined by size exclusion but also by the so-called Donnan exclusion which postulates that ions carrying the same charge as the membrane, i.e., the so-called co-ions, will be excluded from the membrane. The Donnan exclusion is the result of the Donnan potential which is established between the surface of an ion-exchange membrane in equilibrium with an electrolyte solution and the electroneutrality requirement which postulated that on a macroscopic scale positive and negative charges must be compensated. The Donnan potential and Donnan exclusion is discussed in dedicated entries. The Donnan potential between an ion-exchange membrane and a dilute electrolyte solution is given to a first approximation by:

$$\varphi_{Don} = \sum_i \frac{1}{z_i F} \left[RT \ln \frac{{}^s C_i}{{}^m C_i} \right] \quad (6)$$

Here, φ_{Don} is the Donnan potential, ${}^s C_i$ and ${}^m C_i$ are concentration of an ion in the solution and the membrane, respectively.

The exclusion of the co-ions in a dilute solution of a single monovalent electrolyte is given to a first approximation by:

$${}^m C_{co} = \frac{{}^s C_s^2}{C_{fix}} \quad (7)$$

Here, ${}^m C_{co}$, ${}^s C_s$ and C_{fix} are the co-ion concentration in the membrane, the electrolyte concentration in the solution, and the fixed-ion concentration of the membrane.

In nanofiltration, the concentration of the co-ion in the membrane determines the transport of an electrolyte through the membrane because of the electroneutrality requirement, which postulates that on a macroscopic scale in any electrolyte mixture positive and negative charges, must be compensated. Since in nanofiltration there is no electrical current, the fluxes of positive and negative charges must be identical. Thus is:

$$\sum z_i C_i = 0 \text{ and } \sum z_i J_i = 0 \quad (8)$$

Here, C and J are the concentration and the flux in an electrolyte mixture, z is the charge number of the individual components, and the subscripted i refers to the different components in the electrolyte including the fixed ions of the membrane.

As a result of the Donnan exclusion, the partition coefficient for a component between a nanofiltration membrane carrying positive or negative fixed charges and an electrolyte solution depends on two parameters, one is the size exclusion and the other is the Donnan exclusion. It is:

$$k_i = k_{\text{size}} k_{\text{Don}} \quad (9)$$

Here, k_i is the partition coefficient, k_{size} is the contribution of the size exclusion, and k_{Don} the contribution of the Donnan exclusion.

The partition coefficient can be dominated by the size exclusion or the Donnan exclusion depending on the size of the component or the charge density of the membrane and the concentration of charged components in the feed solution. The total value of the partition coefficient is always $0 \leq k \leq 1$.

The Donnan potential between a nanofiltration membrane with fixed charges and the adjacent solution has an additional effect on its separation in nanofiltration. The Donnan potential for a given membrane is proportionally inverse to the concentration of the solution in contact with its surface. Since the concentrations are different at the feed and the permeate side of the nanofiltration membrane, an electrical potential difference across the membrane is established which affects the transport of charged components through the membrane, and an additional term must be introduced

in Eq. 4 to describe the transport of ions. The flux of individual components through a nanofiltration membrane containing fixed positive or negative charges is given by:

$$J_i = {}^m D_i \left[\left(\frac{\bar{V}_i k_{\text{size}} k_{\text{Don}} {}^s C_i}{RT} \frac{dp}{dz} + k_{\text{size}} k_{\text{Don}} \frac{d {}^s C_i}{dz} \right) + \frac{z_i F k_{\text{size}} k_{\text{Don}} {}^s C_i}{RT} \frac{d\varphi}{dz} \right] + L_v k_{\text{size}} k_{\text{Don}} {}^s C_i \frac{dp}{dz} \quad (10)$$

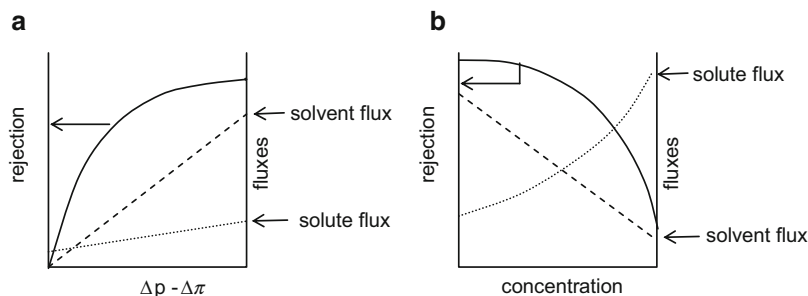
The consequence of the additional driving force of the Donnan potential difference between two solutions separated by a nanofiltration membrane is that components with the same electrical charge such as mono- and divalent cations or anions can be separated when their diffusivity in the membrane is different.

Equation $R_i = \left(1 - \frac{C_i^p}{C_i^f} \right)$ gives the rejection of a certain component in nanofiltration under given operating conditions of applied hydrostatic pressure and feed water composition. The rejection can be calculated from the membrane fluxes by:

$$R_i = 1 - \frac{C_i^p}{C_i^f} = 1 - \frac{J_i}{J_v C_i^f} \quad (11)$$

Here, R_i is rejection of a solute i , C_i^p and C_i^f are the concentration of a solute i in the product and the feed solution, respectively.

For a quantitative determination of the rejection of a certain charged component i , its flux J_i must be known. Therefore, Eq. 10 must be integrated. This, however, is rather difficult because the partition coefficient and the Donnan potential is a function of the feed and permeate electrolyte concentrations. The consequence of the Donnan exclusion and the Donnan potential is that salts can be separated effectively from solutions with neutral components of the same molecular size. The rejection of ions is decreasing with increasing feed solution concentration. In multicomponent electrolyte solutions, ions having different charge numbers and/or different sizes such as mono- and multivalent ions can also be effectively separated by nanofiltration.



Principle of Nanofiltration (NF), Fig. 2 Schematic drawing illustrating the rejection and the solute and solvent flux of an electrolyte through a nanofiltration membrane carrying positive or negative fixed charges (a) at constant

feed concentration as function of the applied hydrostatic pressure and (b) at constant hydrostatic pressure as function of the feed concentration

A quantitative determination of the rejection of nanofiltration membrane as a function of concentration and the applied hydrostatic pressure in multicomponent electrolyte solutions is rather difficult. However, a qualitative treatment and a rational interpretation of experimental results is possible on the basis of the above derived Equations. In Fig. 2, the rejection of a salt by a nanofiltration membrane carrying positive or negative fixed charges at the surface is shown schematically.

Figure 2a indicates that the nanofiltration of an electrolyte solution at constant feed concentration with a membrane carrying fixed surface charges the solvent flux increases linearly with the applied hydrostatic pressure as predicted by Eq. 3. The solute flux, however, increases only marginally with the increasing pressure as indicated by Eq. 10.

Therefore, the rejection will increase with the applied pressure according to a hyperbolic function and approaches its maximum value at infinitely high pressure. At constant pressure, the solvent flux will decrease more or less linearly with increasing feed concentration due to the increase of the osmotic pressure as indicated in Eq. 3. The solute flux increases exponentially with increasing concentration. Therefore, the rejection decreases exponentially with increasing concentration and will become 0 when the osmotic

pressure of the feed solution is equal to the applied hydrostatic pressure.

The qualitative description of the mass transport in nanofiltration based on Eqs. 3 and 10 is well in agreement with experimental results. The mass transport in nanofiltration membrane has also been discussed in the literature in various publications (Wang et al. 1995; Tsuru et al. 1991; Bowen and Mukhtar 1996; Shafer et al. 2005).

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Principle of Pervaporation

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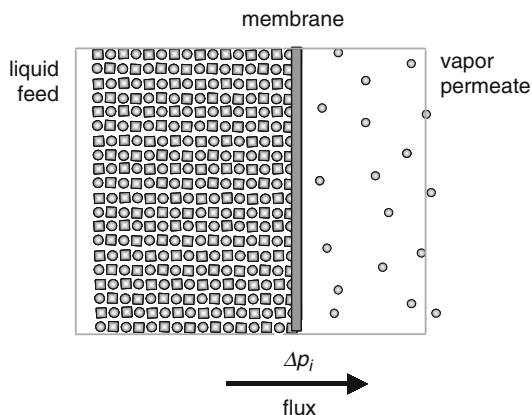
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Synonyms

Mass transfer in PV

Pervaporation is a membrane process in which the permeation of certain components through a membrane from a liquid feed mixture into a vapor phase is combined with the evaporation of these components (Strathmann et al. 2006). The principle of the process is illustrated in Fig. 1.

The membranes and transport mechanism of a component through these membranes used in pervaporation are the same as in gas separation. The driving force for the transport is the chemical potential gradient of the permeating components in the membrane. The chemical potential gradient in the membrane can be related to the partial vapor pressures in the liquid and vapor phase. To establish a partial pressure difference of a component in the liquid and the vapor phase, generally, a vacuum is applied at the permeate side of the membrane. But differences in the partial pressure of a component can also be established by using a sweeping gas on the permeate side or by a



Principle of Pervaporation, Fig. 1 Schematic drawing illustrating the principle of pervaporation showing an asymmetric membrane with a dense solution-diffusion type barrier layer

temperature difference between the liquid feed and the vapor.

The mass transport in a pervaporation membrane can be described by the same mathematical relations as the gas transport with the exception that the chemical potential in the membrane on the feed side of the membrane is not expressed by the molar fraction, the hydrostatic pressure, and the fugacity coefficient but by the molar fraction and the activity coefficient in the liquid phase and the saturation pressure of the component.

Thus, the mass transport in pervaporation is given by:

$$J_i = -D_i k_i \frac{X_i^p p^p - X_i^l \gamma_i^l p_i^0}{\Delta z} \quad (1)$$

Here, D_i is the diffusion coefficient of the component i in the membrane, k_i is the sorption coefficient of the component i into the membrane matrix, X is the molar fraction, p is the pressure, γ is the activity coefficient, the subscripts j and k refer to components of the mixture, and the superscripts o , l , and p refer to saturation pressure, feed, and permeate, respectively.

Equation 1 describes the permeation flux of a component i as a function of the feed and permeate

mixture composition and its diffusivity and solubility in the membrane which can easily be determined by independent measurements. The practical application of Eq. 1, however, is rather limited since the diffusion coefficient as well as the distribution coefficient are not constant but depend strongly on the concentration of the permeating component in the membrane. This dependency must be determined experimentally and may be different for different membrane materials and vapors.

The product of diffusion and distribution coefficient is referred to as permeability coefficient, and the ratio of the permeability coefficients of two components determine the membrane selectivity for the two components.

$$D_i k_i = P_i \quad (2)$$

and

$$S_{j,k} = \frac{P_j}{P_k} \quad (3)$$

Here, P is the permeability of the membrane, S is the membrane selectivity, and j and k refer to the components of the mixture.

The separation factor in pervaporation of a two-component mixture is given by:

$$\alpha_{j,k} = \frac{X_j^p X_k^p}{X_j^l X_k^l} = S_{j,k} \frac{X_j^p \varphi_j^p - X_j^l \gamma_j^l p_j^0}{X_k^p \varphi_k^p - X_k^l \gamma_k^l p_k^0} \frac{X_k^l}{X_j^l} \quad (4)$$

Here, α is the separation factor, S is the membrane selectivity, X is the molar fraction, p is the pressure, γ is the activity coefficient, the subscripts j and k refer to components of the mixture, and the superscripts o , l , and p refer to saturation pressure, feed, and permeate, respectively.

In pervaporation, the partial pressure of the components on the permeate side is kept as low as possible by either using a sweeping gas or more commonly by applying a vacuum, i.e., $X_j^p p^p \ll X_j^l \gamma_j^l p_j^0$ and $X_k^p p^p \ll X_k^l \gamma_k^l p_k^0$. For a pervaporation experiment using a vacuum, the separation factor is to a first approximation:

$$\lim_{p^p \rightarrow 0} \alpha_{j,k} = S_{j,k} \frac{\gamma_j^l p_j^0}{\gamma_k^l p_k^0} \quad (5)$$

It should be noticed that the separation factor consists of two terms, the first term, i.e., $S_{j,k}$, represents the membrane selectivity, and the second term, $\frac{\gamma_j^l p_j^0}{\gamma_k^l p_k^0}$, the thermodynamic liquid/vapor equilibrium which represents the separation that would be achieved by distillation. In pervaporation, the membrane selectivity can increase or decrease the distillation selectivity and eventually push the overall separation factor into the opposite direction.

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Principle of Reverse Osmosis (RO)

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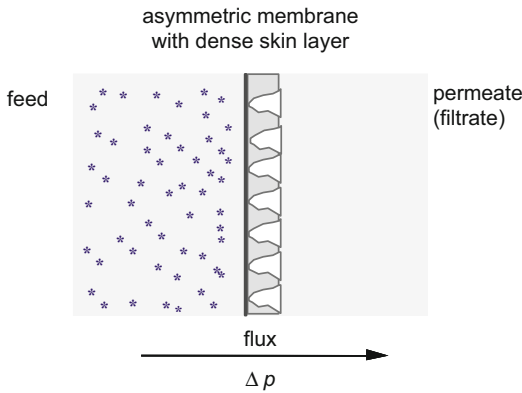
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Synonyms

Mass transfer in Reverse Osmosis RO



Principle of Reverse Osmosis (RO), Fig. 1 Schematic drawing illustrating the principle of reverse osmosis

In reverse osmosis the driving force is also a hydrostatic pressure difference. The principle of the process is illustrated in Fig. 1, which shows a solution containing a low molecular weight component separated by a membrane from the solvent and a hydrostatic pressure difference applied across the membrane resulting in a flux of solvent from the solution into the pure solvent (Strathmann et al. 2006).

The membrane used in reverse osmosis has an asymmetric structure with a dense barrier layer at the side facing the feed solution. It is assumed that in this layer the individual components are transported by diffusion and that viscous flow through pores or pinholes can be neglected. For describing the transport in reverse osmosis membranes two approaches are described in the literature. One is the so-called solution-diffusion model which neglects kinetic coupling of different fluxes (Merten 1966). The second is based on the phenomenological equation of the thermodynamic of irreversible processes (Katchalsky and Curran 1967). This model does consider kinetic coupling between different fluxes. Both models describe the transport in reverse osmosis membranes quite accurately indicating that kinetic coupling is not of great importance in reverse osmosis.

Reverse Osmosis Mass Transport Described by the Solution-Diffusion Model

In the solution-diffusion model, the flux of different components through a membrane is assumed to be

by diffusion only and can be described by the product of its concentration and mobility in the membrane matrix and the chemical potential gradient of the component in the membrane. Furthermore, it is assumed that there is no kinetic coupling between fluxes, that the volume flux is approximately identical to the flux of the solvent, and that the solute flux due to the pressure gradient is negligibly small compared to the solute flux due to the activity gradient.

Thus, the flux of a component in the membrane can be described by:

$$J_i = L_i d\mu_i = L_i (\bar{V}_i dp + RT d\ln a_i) \\ = \frac{D_i^m C_i}{RT} (\bar{V}_i dp + RT d\ln a_i) \quad (1)$$

Here, J is the flux, L is phenomenological coefficient, μ is the chemical potential, p is the hydrostatic pressure, a is the activity, $\bar{V}$ is the partial molar volume, D is the diffusion coefficient, and $^m C_i$ is the concentration in the membrane; the subscript i refers to a component.

For the solvent, i.e., $i = w$ it is assumed that $J_v \cong J_w$ and $C_w \bar{V}_w = 1$. For the solute, i.e., $i = s$ it is assumed that: $d\mu_s \cong RT d\ln a_s$ and $\pi \cong \frac{RT \ln a_w}{\bar{V}_w}$. Here the subscripts v , w , and s refer to volume, solvent, and solute.

Integrating over the cross section of the membrane and expressing the activity of the solvent by the osmotic pressure and that of the solute by its concentration gives the volume flux to:

$$J_v = L_w \bar{V}_w^2 (\Delta p - \Delta \pi), \quad (2)$$

and the solute flux to:

$$J_s = D_s^m C_s d\ln^m C_s = D_s d^m C_s \quad (3)$$

The concentration of the different components in the membrane is proportional to the concentration in the outside solutions and it is given by:

$$^m C_i = k_i C_i \quad (4)$$

Here, k_i is the partition coefficient of the component i between the membrane and the adjacent solution, C_i and $^m C_i$ are the concentrations in the outside solution and in the membrane.

Introducing Eq. 4 into Eqs. 2 and 3 gives the volume flux, i.e., the filtration rate, and the flux of the solute as function of the applied hydrostatic pressure, the osmotic pressure, the diffusion coefficient of a component in the membrane, its concentration in the feed and permeate solution, and its partition coefficient between the membrane and the feed solution:

$$\begin{aligned} J_v &= \frac{k_w D_w C_w \bar{V}_w^2}{RT} (\Delta p - \Delta \pi) \\ &= \frac{k_w D_w \bar{V}_w}{RT} (\Delta p - \Delta \pi) \end{aligned} \quad (5)$$

and

$$J_s = k_s D_s (C_s^f - C_s^p) \quad (6)$$

Here, J_v is the volume flux, J_s is the solute flux, D is the diffusion coefficient, k is the partition coefficient of the components between the membrane and the adjacent solutions, C is the concentration, p the hydrostatic pressure, and π the osmotic pressure of the solutions, the subscripts s and w refer to solute and water, respectively, and the superscripts m , f , and p refer to the membrane, the feed, and the permeate. Furthermore is $V_w C_w = 1$.

To determine the rejection, the Eqs. 5 and 6 are introduced into Equation $R_i = \left(1 - \frac{C_i^p}{C_i^f}\right)$. Thus is:

$$\begin{aligned} R_s &= 1 - \frac{C_s^p}{C_s^f} = 1 - \frac{J_s}{J_v C_s^f} \\ &= 1 - \frac{k_s^m D_s (C_s^f - C_s^p) RT}{k_w^m D_w \bar{V}_w (\Delta p - \Delta \pi) C_s^f} \end{aligned} \quad (7)$$

Equation 7 shows that rejection of a component in reverse osmosis is not only a function of the membrane and feed solution properties it is also a function of the applied hydrostatic pressure. The rejection will increase with increasing applied hydrostatic pressure and approaches asymptotically a maximum value.

Reverse Osmosis Transport Described by the Phenomenological Equations

In deriving Eqs. 5, 6, and 7 on the solution diffusion model, a number of assumptions have been made including the neglecting of all kinetic coupling between transported components and any viscous flow. A more comprehensive treatment of the mass transport in reverse osmosis membranes, where kinetic coupling and convective flow are taken into account, is based on phenomenological equations applied to the laws of the thermodynamic of irreversible processes. In a reverse osmosis system, which consists of a membrane and a two component feed solution, i.e., a solvent and a solute, two independent fluxes will be obtained when the membrane is used as frame of reference. These fluxes can be described by:

$$J_i \sum_k L_{ik} X_k (i, k = 1, 2, 3 \dots, n) \quad (8)$$

Here, J is the flux of the different components, L is the phenomenological coefficient, and X is the driving force, the subscripts i and k refer to different components.

Assuming a system without viscous flow composed of a solute, a solvent, and a membrane as frame of reference there are two independent fluxes:

$$J_w = L_w d\mu_w + L_{ws} d\mu_s \quad (9)$$

and

$$J_s = L_{sw} d\mu_w + L_s d\mu_s \quad (10)$$

Here, J is the flux, μ is the chemical potential, L is the phenomenological coefficient, the subscripts w and s refer to the solvent which is assumed to be water and the solute which is assumed to be salt, the subscripts ws and sw refer to the coupling between the fluxes of water and salt and salt and water.

The diagonal coefficients L_w and L_s are always positive while coupling coefficients L_{sw} and L_{ws} can be positive or negative as can be seen from the dissipation function which describes the entropy production in a process. The total number of coefficient in the phenomenological equations is

reduced by the Onsager relation, which postulates that the coupling coefficients L_{sw} and L_{ws} are identical (Onsager 1931a, b). However, Eqs. 9 and 10 are not very useful to describe the transport properties of a reverse osmosis membrane because the coupling coefficients are difficult to determine in an independent measurement and generally in reverse osmosis the total filtration rate, i.e., the volume flux is of interest. However, the coupling coefficient can be converted to more easily measurable constants when the phenomenological equations are slightly modified by introducing the volume flux and a diffusive flux (Kedem and Katchalsky 1961).

The dissipation function for the Eqs. 9 and 10 is given by:

$$\begin{aligned}\Psi &= J_w d\mu_w + J_s d\mu_s \\ &= J_w d(\bar{V}_w p + RT \ln a_w) \\ &\quad + J_s d(\bar{V}_s p + RT \ln a_s)\end{aligned}\quad (11)$$

Here, ψ is the dissipation function, J is the flux, a , μ , and $\bar{V}$ are the activity, the chemical potential, and the partial molar volume, and p is the hydrostatic pressure, the subscripts w and s refer to solvent and solute.

Assuming a linear relation for the chemical potential gradients and introducing the osmotic pressure for the activities of the water and solute integration of Eq. 11 lead to:

$$\begin{aligned}\Psi &= (J_w \bar{V}_w + J_s \bar{V}_s) \Delta p \\ &\quad + \left(\frac{J_s}{C_s} - J_w \bar{V}_w \right) \Delta \pi \\ &= J_v \Delta p + J_D \Delta \pi\end{aligned}\quad (12)$$

Introducing a volume and a diffusion flux given by:

$$J_v = J_w \bar{V}_w + J_s \bar{V}_s \quad (13)$$

and

$$J_D = \frac{J_s}{C_s} - \bar{V}_w J_w \quad (14)$$

into the dissipation function results in:

$$\Psi = J_v \Delta p + J_D \Delta \pi \quad (15)$$

The first term in Eq. 15 describes the total volume flux J_v as function of the applied pressure, and the second term describes the diffusion flux of the salt J_D .

The new set of phenomenological equations is:

$$J_v = L_p \Delta p + L_{pD} \Delta \pi \quad (16)$$

and

$$J_D = L_{Dp} \Delta p + L_D \Delta p + L_D \Delta \pi \quad (17)$$

By applying different experimental conditions to the Eqs. 16 and 17, the phenomenological coefficients can be determined from experimental measurements.

Assuming no pressure difference is applied, i.e., $\Delta p = 0$, then the diffusive flux is given by:

$$(J_D)_{\Delta p=0} = L_D \Delta \pi \quad (18)$$

and the volume flux is given by:

$$(J_v)_{\Delta p=0} = L_{pD} \Delta \pi \quad (19)$$

Assuming that there is no osmotic pressure difference, i.e., $\Delta \pi = 0$, then the diffusive flux is given by:

$$(J_D)_{\Delta \pi=0} = L_{Dp} \Delta p \quad (20)$$

and the volume flux is given by:

$$(J_v)_{\Delta \pi=0} = L_p \Delta p \quad (21)$$

The hydrostatic pressure difference at zero volume flux, i.e., the osmotic equilibrium is given by:

$$(\Delta p)_{J_v=0} = -\frac{L_{pD}}{L_p} \Delta \pi = \sigma \Delta \pi \quad (22)$$

Here, σ is the so-called Staverman reflection coefficient which is a measure for the permselectivity of a membrane.

Equation 22 shows that in osmotic equilibrium the hydrostatic pressure difference between two solutions separated by a membrane is equal to the osmotic difference $L_p = L_{pD}$ and therefore $\sigma = 1$.

This is only the case for a strictly semipermeable membrane. Usually, the Staverman reflection coefficient has values between 0 and 1.

If the volume flux is 0, the ratio of salt flux to osmotic pressure difference is given by:

$$\left(\frac{J_s}{\Delta\pi}\right)_{J_v=0} = \frac{C_s L_p L_D - L_{pD}^2}{L_p} = \omega \quad (23)$$

Here, ω is the permeability of the salt.

Combining Eqs. 13, 14, 18, 22, and 23 leads to:

$$J_v = L_p(\Delta p - \sigma \Delta\pi) \quad (24)$$

and

$$J_s = C_s(1 - \sigma)J_v + \omega \Delta\pi \quad (25)$$

Based on the phenomenological equations, the mass transport in reverse osmosis of a solution of a single salt solution can be described by three coefficients, i.e., L_p the hydrodynamic permeability of the membrane, ω the salt permeability, and σ the reflection coefficient. All three coefficients can be experimentally determined.

Comparing Eqs. 24 and 25 with Eqs. 5 and 6 which are based on the solution-diffusion model that for membrane with high salt rejection, i.e., $\sigma \approx 1$ and when kinetic coupling between the water and the salt flow is low which can be assumed in most reverse osmosis membranes the transport in reverse osmosis can adequately be described by the solution-diffusion model.

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Principle of Ultrafiltration (UF)

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Synonyms

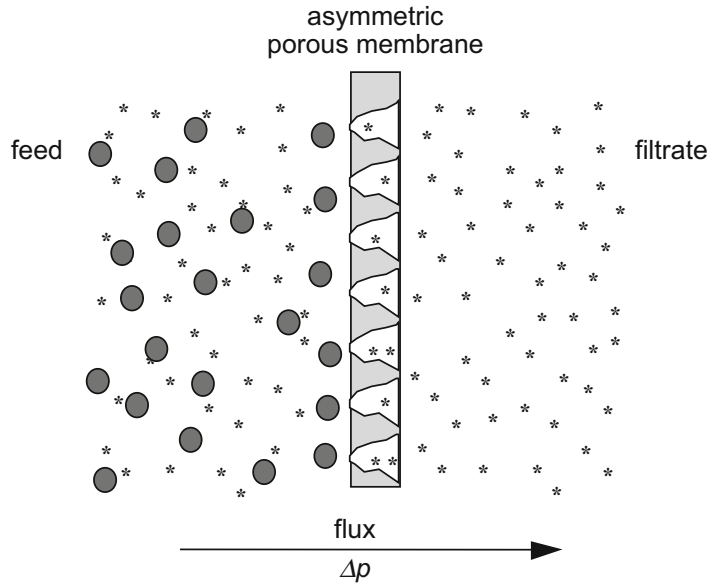
Mass transport in ultrafiltration

In ultrafiltration (UF) the driving force is a pressure gradient and the mass transport is dominated by the convective flux through pores (Strathmann et al. 2006). The principle of the process is depicted in Fig. 1.

As in microfiltration a porous membrane and a hydrostatic pressure difference is applied to separate certain components from a feed solution. However, the structure of an ultrafiltration membrane is asymmetric having the smallest pores on the surface facing the feed solution, and its pores are significantly smaller than those of a microfiltration membrane. Its diameters at the feed side surface of the membrane are between 2 and 10 nm, and the components retained by an ultrafiltration membrane have a molecular weight between 5,000 to several million Dalton. Since

Principle of Ultrafiltration (UF),

Fig. 1 Schematic drawing illustrating the principle of ultrafiltration



ultrafiltration membranes retain also some relatively low molecular weight solutes, osmotic pressure differences between the feed and the filtrate can be significant and diffusive fluxes of the solutes across the membrane are no longer negligibly low. Therefore, the flux of individual components in ultrafiltration can be expressed as a function of a hydrostatic pressure and a difference in the chemical potential of the different components between the feed and filtrate solutions. The volume flux, i.e., the filtration rate, is given by the sum of the fluxes of the individual components:

$$J_v = \sum_i J_i \bar{V}_i = \sum_i \bar{V}_i L_i \frac{d\mu_i}{dz} + L_v \frac{dp}{dz}$$

$$= \sum_i \bar{V}_i L_i \frac{d}{dz} (\bar{V}_i p + RT \ln a_i) + L_v \frac{dp}{dz} \quad (1)$$

Here J is the flux, L is a phenomenological coefficient referring to interactions of the permeating components with the membrane matrix, $\bar{V}_i$ is the partial molar volume, μ is the chemical potential, p is the hydrostatic pressure, z is a directional coordinate, a is the activity, and the subscripts v and i refer to volume flow and individual components.

The first term in Eq. 1 describes the diffusive fluxes of all components in the pores of the membrane and the second term the volume flow.

In ultrafiltration the total volume flux, i.e., the filtration rate in a dilute solution, can be expressed to a first approximation by the flux of the solvent, i.e., $J_v \cong J_w$, and the activity of the solvent in the solution a_w can be expressed by an osmotic pressure. Assuming a linear relation for the pressure and activity gradients across the membrane, integration of Eq. 1 gives the flux through an ultrafiltration membrane as a function of pressure difference between feed and permeate solution, the hydrodynamic permeability for the viscous flow, the osmotic pressure difference between feed and permeate solution, and the phenomenological coefficient determining the diffusive flow of water through the membrane pores:

$$J_v \cong J_w = \bar{V}_w^2 L_w \frac{\Delta p - \Delta \pi}{\Delta z} + L_v \frac{\Delta p}{\Delta z} \quad (2)$$

Here J_v and J_w are total volume and solvent fluxes, respectively, Δp and $\Delta \pi$ are the hydrostatic and the osmotic pressure gradients across the membrane, L_v is the hydrodynamic permeability, L_w is the diffusive permeability of the solvent, and Δz is the thickness of the selective barrier of the membrane.

In most practical applications of ultrafiltration, the first term of Eq. 2 can be neglected since $L_w \ll L_v$. The osmotic water transport will affect the membrane volume flux only when the

difference in osmotic pressure between the feed and permeate solution is significantly higher than the hydrostatic pressure difference. This is only the case for ultrafiltration of solutions containing a high concentration of retained components of relatively low molecular weight. Since generally only macromolecular components are retained, the volume flux, i.e., the filtration rate in ultrafiltration, can be described to a first approximation by

$$J_v = L_v \frac{\Delta p}{\Delta z} \quad (3)$$

For the transport of solutes through an ultrafiltration membrane, the diffusive flux can generally not be neglected and the flux of the solute through the membrane can be expressed as the sum of a diffusive flux due to a chemical potential driving force and a convective flux due to the concentration in the pore solution:

$$J_i = L_i \frac{d}{dz} (\bar{V}_i p + RT \ln a_i) + L_v {}^m C_i \frac{dp}{dz} \quad (4)$$

Here ${}^m C_i$ is the concentration of the solute in the pore solution.

It can be shown that for hydrostatic pressure, differences usually applied in ultrafiltration is: $\bar{V}_i p \ll RT \ln a_i$. If it is assumed that the activity coefficient of the solutes in the membrane is 1, the phenomenological coefficient can be expressed by the Fick's diffusion coefficient according to equation $J_i = -D_i \frac{dC_i}{dz}$. Introducing these approximations into Eq. 4 leads to

$$J_i = J_v {}^m C_i - {}^m D_i \frac{d {}^m C_i}{dz} \quad (5)$$

Integration of Eq. 5 over the membrane thickness gives

$$J_i = J_v \frac{{}^m C_i^f \exp \frac{J_v \tau \Delta z}{{}^m D_i} - {}^m C_i^p}{\exp \frac{J_v \tau \Delta z}{{}^m D_i} - 1} \quad (6)$$

Here J is the flux, C is the concentration, D is the diffusion coefficient, τ is the tortuosity factor, and Δz is the thickness of the membrane; the subscripts

i and v refer to solute and the volume; the superscripts m , f , and p refer to the membrane, the solution in the membrane at the feed side, and the solution in the membrane at the permeate side.

Equation 6 shows that the flux of a component i which is partly retained by the membrane in ultrafiltration consists of two terms. The first term represents the viscous flow and is a linear function of the hydrostatic pressure. The second term represents the diffusion in the pore liquid and is an exponential function of the hydrostatic pressure.

In ultrafiltration there are two limiting cases for the transport mechanism. In the first case, it is assumed that if the hydrostatic pressure and thus the viscous flow is zero, then the transport of a solute is determined by diffusion only, i.e.,

$$\lim_{J_v \rightarrow 0} J_i = 0 \quad (7)$$

The second limiting case is obtained when the pressure and thus the viscous flow is infinitely high. Then the transport of the solute is determined by its concentration in the membrane, i.e.,

$$\lim_{J_v \rightarrow \infty} J_i = J_v {}^m C_i^p \quad (8)$$

Since the flux of the solute in ultrafiltration is a function of the viscous flux, the retention of an ultrafiltration membrane is obviously a function of the applied hydrostatic pressure. It can be described by combining equation

$R_i = \left(1 - \frac{C_i^p}{C_i^f}\right)$ and Eq. 6 and by introducing partition coefficients to relate the concentrations of the solute in the feed and the permeate to that in the membrane. Thus is

$$R_i = 1 - \frac{k^f \exp \frac{J_v \tau \Delta z}{{}^m D_i}}{k^p - 1 + \exp \frac{J_v \tau \Delta z}{{}^m D_i}} \quad (9)$$

with

$$k^f = \frac{{}^m C_i^f}{C_i^f} \quad \text{and} \quad k^p = \frac{{}^m C_i^p}{C_i^p} \quad (10)$$

Here k_f and k_p are the partition coefficients which relate the concentrations in the feed and the permeate to that in the membrane. In most ultrafiltration membranes, the two partition coefficients are identical.

The effect of the hydrostatic pressure on the retention in ultrafiltration becomes more clear when two extreme cases are considered, i.e., a very large and a very small hydrostatic pressure difference between the feed and the permeate solution. At large pressure differences, the viscous flux is high and the retention approaches a maximum value which is determined by the distribution coefficient of the solute between the membrane and the solution:

$$\lim_{J_v \rightarrow \infty} R_i = 1 - k^f \quad (11)$$

At very low hydrostatic pressure the retention goes to zero:

$$\lim_{J_v \rightarrow 0} R = 0 \quad (12)$$

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Process Control in Membrane Operations

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Efficient automatic control system is an essential part of every plant being operated in chemical industry. It may be implemented for various reasons: plant and environmental safety, fulfillment of varying process demands, rejection of input disturbances, optimal production desire, etc.

Process control is usually achieved via feedback policy. By measuring time-varying process outputs $y(t)$ (controlled variables), such as temperature or concentration, one decides about process inputs $u(t)$ (manipulated variables), such as input power to heating cell or valve position, to attain some or all of the abovementioned goals.

Classical control theory defines a fashion in which obtained measurements are used to identify value of input as a control law. Its basic form can be stated as

$$u(t) = f(y(t))$$

where $f(\cdot)$ represents a function which can take various forms and can be designed using analytical or numerical methods in order to establish optimal, adaptive, robust, stochastic, or any other type of process control.

Process control can be designed by exploiting neural network or fuzzy logic approach. The latter technique was used to control microfiltration process by Perrot et al. 1996.

However, the most popular control applications are accompanied with the use of proportional-integral-derivative (PID) controller. Its control law can be written as

$$u(t) = K_p e(t) + K_i \int_0^t e(\tau) d\tau + K_d \frac{d}{dt} e(t)$$

where K_p , K_i , and K_d are proportional, integral, and derivative gains, respectively, and $e(t)$ represents control error, a difference between desired and actual value of the output. There are numerous applications of PID controller in membrane technology and processes (van Reis et al. 1997; Smith et al. 2005; Blankert et al. 2007; Yee et al. 2008).

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Productivity and Footprint in Gas Separation

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The productivity to footprint compares the productivity of the separation system with respect to the installation area occupied by the system itself (Eq. 1) (Criscuoli and Drioli 2007). Considering the same area occupied by the units, this metric identifies the most productive scheme to get a set target. Future plants should be characterized by high productivities and low sizes; therefore, a high value of this index is highly desired.

To compare two different technologies that can be used for the same separation, the ratio between the values of productivity/footprint ratio obtained for each of them can be defined (Eq. 2). When the value of this ratio is higher than 1, membrane operations should be preferred, whereas, for values lower than 1, traditional units should be chosen.

$$\text{Productivity}_i/\text{Footprint} = \frac{\text{Productivity}}{\text{Footprint occupied by the installation}} \quad (1)$$

Productivity footprint ratio

$$= \frac{(\text{Productivity}_i/\text{Footprint})^{\text{Membranes}}}{(\text{Productivity}_i/\text{Footprint})^{\text{Traditional technology}}} \quad (2)$$

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Propane Oxidative Dehydrogenation by Membrane Reactor

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Propene is industrially obtained in naphtha crackers, in FCC units, and in a growing proportion, by dehydrogenation of propane. Propane dehydrogenation is an endothermic reaction, and the maximum achievable conversion is limited by thermodynamic equilibrium. An alternative to propane dehydrogenation is the oxidative dehydrogenation of propane. In such case, the reaction is irreversible, but the inconvenience is the appearance of nonselective oxidation reactions of propane and propene to carbon oxides (CO and CO₂). The success of propane oxidative dehydrogenation will be linked to the achievement of high selectivity to propene and high enough conversion (Cavani et al. 2007). A large amount of research has been devoted to the optimization of the catalyst, and this is obviously a key factor, but the selection of a suitable reactor may be another factor contributing to achieve a successful result. A packed bed membrane reactor in which propane is fed at the catalyst bed entry and oxygen is permeated along the membrane provides a low partial pressure of oxygen in the reaction zone. For many catalysts, a low partial

pressure of oxygen implies a better selectivity to propene (Ziaka et al. 1993; Pantazidis et al. 1995; Tonkovich et al. 1996). The use of porous membranes has been reviewed by Coronas and Santamaría (1999) and Julbe et al. (2001).

Modifications in the Reactor Configuration

This approach has been employed by several researchers with a variety of modification in the configuration:

- Pure propane and homogenous oxygen distribution along the bed.
- Propane diluted with inert gas and/or oxygen diluted with inert gas. In comparison with the previous approach, safety is increased and often the selectivity achieved is better, but the industrial application would require the separation of inert gases from the reaction products, increasing the process operation costs.
- Nonhomogenous distribution of oxygen feed. In order to obtain a greater reaction rate at the reactor entry, a larger permeation of oxygen near the propane entry may be useful.
- Combination of a conventional fixed bed reactor with a membrane reactor. In such case, the feed to the fixed bed reactor contains a small amount of oxygen.
- The use of a catalytic membrane. In this case, part of the membrane is loaded with catalyst, preferentially in the side where propane is fed. The operation principle is the same as when a packed bed of catalyst is employed: the lower oxygen partial pressure in the reaction zone increases the selectivity to the desired product (Alfonso et al. 1999; Julbe et al. 2000).

Types of Membrane

The membrane employed for this reaction does not need to be selective for oxygen, i.e., a mesoporous membrane may be employed. In such case, the back permeation of hydrocarbon to the shell side must be avoided. This usually requires a significant

pressure drop of oxygen. Examples of membranes employed include microfiltration ceramic membranes with the pores filled with silica, nanofiltration ceramic membranes with enamel trips to reduce the permeation or zeolite membranes. In an alternative configuration, the membrane has catalytic activity (Alfonso et al. 1999).

Alternatively dense ceramic membranes, i.e., oxygen selective, can be employed (Wang et al. 2003; Czuprat et al. 2010). In such case, in addition to the improvement in propene selectivity provided by the oxygen distribution and the avoidance of back permeation problems, the previous step of oxygen separation from air may be avoided.

Catalysts

Although in principle any catalyst suitable for oxidative dehydrogenation of propane could be tested in propane dehydrogenation, the most employed are the simplest ones: vanadium oxide supported on alumina or on magnesium oxide.

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Propolis Extract Nanofiltration

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Propolis is a mixture of beeswax and resins collected by the honeybee from plants, particularly from flowers and leaf buds. Its composition depends on the type of plants accessible to the bees. There are changes in color, odor, and probably medicinal characteristics according to source and the season of the year. The major compounds are resins composed of flavonoids and phenolic acids or their esters, which often form up to 50 % of all ingredients. The variation in beeswax content also influences the chemical analysis. More than 500 different compounds from propolis through several regions were isolated, being impossible to determine their composition without first analysis.

Propolis composition is responsible for a lot of studies relating antimicrobial, antioxidant, anticarcinogenic and antifungal activities, among other health benefits. Thanks to these

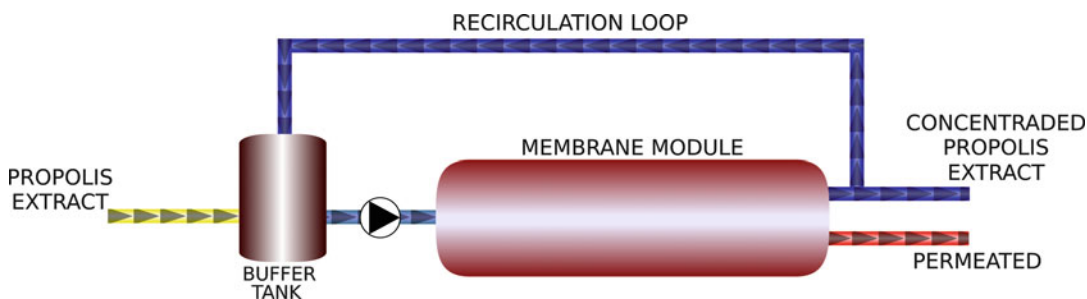
characteristics, a great interest exists to use propolis for human consumption as being incorporated in drugs, cosmetics, and foods.

The most usual way to manipulate propolis is by its extract. Ethanol is the most common solvent used once it can extract the major constituents from propolis at low cost. Other solvents as water and propylene glycol are also studied.

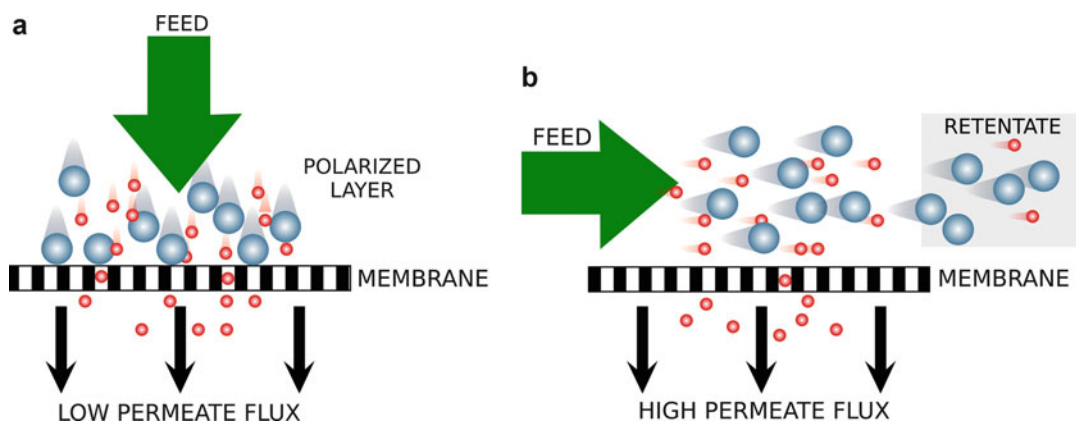
The excess of solvents in extracts can be responsible for some limitation in industrial process, causing some variation in the final product, so it is necessary to concentrate it before use. The most traditional methods are lyophilization (freeze-drying), vacuum distillation, evaporation, and distillation. These methods require a high energy consumption and in some cases high temperatures that can degrade some functional compounds. To avoid these drawbacks, the method of nanofiltration has been studied for propolis concentration (Fig. 1).

Nanofiltration membranes are the same as reverse osmosis membranes; only the network structure is more open, causing a lower retention of monovalent salts (Mulder 1996). It has been widely used in concentration process where the objective is to retain functional compounds with low molecular weight, especially phenolic compounds.

Propolis nanofiltration has been studied for some authors recently, and the process showed a high efficiency in retaining flavonoids and phenolic compounds, which are of major importance to propolis quality, reaching more than 95 % rejection in concentration factor of 3.0 and 4.0. Moreover, the process had low fouling and concentration polarization, phenomena that can



Propolis Extract Nanofiltration, Fig. 1 Schematic diagram of propolis extracts nanofiltration process



Propolis Extract Nanofiltration, Fig. 2 Differences between conventional (a) and tangential filtration (b)

make the whole process inviable through flux decay (Tylkowski et al. 2010; Mello et al. 2010).

Application of this technology could increase the use of propolis in many industrial applications, in new research projects, and in the development of new products with functional properties. Furthermore, this process allows removal of the solvent from the extract, reducing the disadvantages associated with using alcoholic extractions, and being feasible the use of another solvent during extraction procedure. In the membrane process, the product is not submitted to high temperatures, and there is no change in the physical state of the solvent, which means that the functional properties of the compounds of interest are preserved and the process as a whole is energy saving.

Cross-flow nanofiltration experiments showed that the nanofiltration process can be feasible technology for medicine and nutritional additive production based on propolis extracts (Fig. 2).

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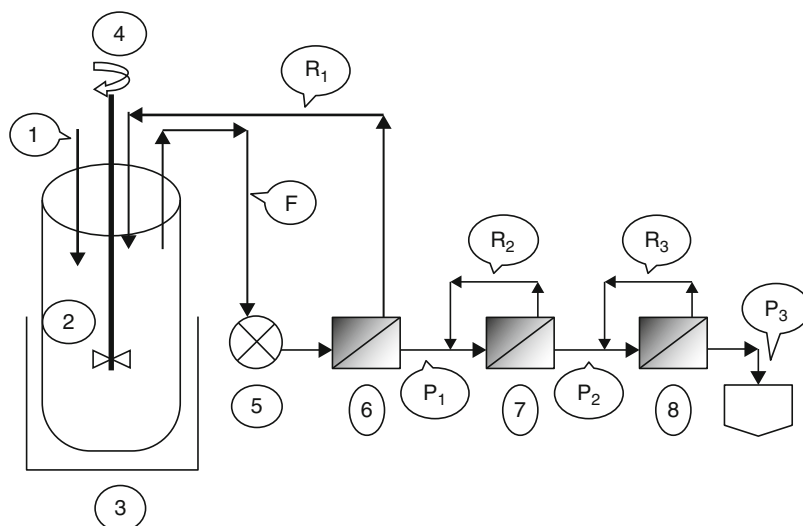
Proteases in Membrane Bioreactor

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Protease (also termed peptidase/proteinase) refers to a group of enzyme system that conducts the protein catabolism by hydrolysis of the peptide bonds between composing amino acids in polypeptide chain forming protein.

The modification of protein by protease offers synthesis of a wide range of value-added compounds with improved functionality from diverse sources. The protein with little commercial values (yellow fin sole frame, alfalfa protein, sea cucumber gelatin) can be converted to value-added products (bioactive peptides) by enzymatic modifications (Jung et al. 2006; Kapel et al. 2006; Zhao et al. 2007). Depending on enzyme-substrate binding site in the polypeptide chain, the protease system is classified as exoprotease (side peptide bonds) and endoprotease (inner polypeptide bonds). The type of protease in effect (serine protease, threonine protease, cysteine protease, aspartate protease, glutamic protease, metalloprotease) decides the nature of amino acids at the side chain of the product peptides. The end use of the hydrolyzed protein fragment (peptides) specifies the protease type in use.



Proteases in Membrane Bioreactor,

Fig. 1 Operational set up for hydrolysis of sesame protein isolate in EMR (side stream recycle membrane bioreactor) and subsequent UF fractionation. 1 feeding line for protein isolate, 2 reaction vessel, 3 constant temperature bath, 4 stirrer, 5 peristaltic pump, 6 cross flow UF with 5kDa

membrane, 7 UF with 2kDa membrane, 8 UF with 1kDa membrane, F - feed, P_1 , P_2 , P_3 permeates, R_1 , R_2 , R_3 retentate (Reprinted from Enzyme membrane reactor in isolation of antioxidative peptides from oil industry waste: A comparison with non-peptidic antioxidants, Das et al. (2012), with permission from Elsevier)

Involvement of protease as catalyst for bioconversion is becoming favorable from consumer acceptance viewpoint and mild reaction condition. Though the enzyme systems have untarnished safety evidence, governmental legislation and regulatory agencies restrict the incorporation of enzymes as food additives, which have motivated the pharmaceutical and food processing industries to develop methods of efficient enzyme separation from reaction mixture that have subsequently raised the concepts of membrane bioreactor.

Membrane bioreactor combines reaction vessel and separation unit in a single piece of equipment in order to obtain the desired product profile of defined molecular sizes. The enzymatic membrane bioreactor (EMR) integrates the enzymatic reactions, product separation, and catalyst recovery in a single operational step. Membrane bioreactor helps to maintain the desired molecular size of the product by proper selection of membrane pore characteristics while the extent of reaction is controlled by residence time in the reactor. They do have implicit advantages since the enzyme is recovered and reused, which leads

to high productivity and increases enzyme utilization (weight of product per unit weight of enzyme) (Cheryan 1998, p. 454), reduces the possibility of enzyme inhibition by hydrolyzates (in case of enzymatic hydrolysis), and improves product purity. In addition, membrane process eliminates the side effect associated with other hydrolysis unit operations, since high temperature is not required for enzyme inactivation. In EMR, protease application for plant protein modification appears tricky due to the presence of unhydrolysable component (hydrophobic core in plant protein) in the feed, which lengthens the reaction time causing unfavorable substrate depletion and product inhibition.

The choice of membrane and membrane bioreactor configuration depends on the nature of desired products and properties of reaction system (substrate and catalyst). Among the usable standard membrane bioreactor configurations (submerged membrane reactor, recycle membrane reactor, and plug flow bioreactor), MBR with external ultrafiltration unit (recycle type) (Fig. 1) is advantageous for protease system to obtain the peptides as desired product, as the substrate and

Proteases in Membrane Bioreactor, Table 1 Application of protease in membrane reactors (Reprinted from Enzyme membrane reactor in isolation of antioxidative peptides from oil industry waste: A comparison with non-peptidic antioxidants, Das et al. (2012), with permission from Elsevier)

Name of protease	Substrate	Membrane reactor configuration	Application profile	References
Alcalase	Casein	Continuous stirred tank membrane reactor	Bioactive peptides	Mannheim and Cheryan (1990)
Protease	Fish protein	Free enzyme membrane bioreactor	Bioactive peptides	Nakajima et al. (1992)
Trypsin	Caseino macropeptide	Continuous submerged EMR	Antithrombotic peptides	Bouhallab and Touzé (1995) Prate-vidal et al. (2001)
Alcalase, flavourzyme, trypsin, chymotrypsin, and pepsin	Soy protein	Continuous spiral-wound (SW) membrane reactor system	Angiotensin-I-converting enzyme inhibitor	Chiang et al. (1999) Chiang et al. (2006)
Trypsin, chymotrypsin	Milk protein	Asymmetric hollow fiber membrane	Baby food	Giorno and Drioli (2000)
Papain	Collagen, mussel protein	CSTR with UF	Meat tenderization	Giorno and Drioli (2000)
Protease N (EC 3.4.24.28)	Whey	Tangential flow filter membrane reactor	Different peptides	Cheison et al. (2006)
<i>Subtilisin carlsberg</i> (E.C. 3.4.21.62)	Alfalfa protein	Continuous EMR	Antihypertensive peptide	Kapel et al. (2006)
Subtilisin protex 6L	Whey	Cyclic batch membrane reactor	Reduced-antigenicity whey protein hydrolysates	Prieto et al. (2007) Prieto et al. (2010)
Protease A Amano 2G	Sesame protein	Semibatch recycle membrane reactor	Peptides with antioxidant activity and bacteriostatic activity	Das et al. (2012)
Alcalase	Wheat germ protein	Continuous coupling of enzymatic hydrolysis and membrane separation	ACE- Inhibitory peptides	Qu et al. (2013)
Porcine pancreatin	Bovine casein	Recycle MBR	Multifunctional peptides	Wu et al. (2013)

biocatalyst are of the same order of magnitude and product and substrate are vastly different in magnitude (Cheryan 1998, p. 451) (Rios et al. 2004).

The earliest demonstration of membrane bioreactor concept was by Blatt et al. (1968) for hydrolysis of milk protein with α -chymotrypsin in dead-end stirred cells reactor. Cheison et al. (2011) has given a detailed list of the various proteins hydrolyzed in EMR including several plant proteins (cotton seed protein, soy protein, corn gluten meal, and sesame protein); animal proteins (fish skin, cod frame protein, yellow fin sole frame, alaska pollock skin, hoki frame

protein, fish collagen); and mammalian proteins (beef rump, milk, eggs, goat whey, casein, hemoglobin, bovine skin gelatin, bovine hoof and horn, and bovine colostrums). Modern utilization pattern implies EMR as a tool of continuous production of specific bioactive peptides (Table 1).

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Protein Crystallization by Membrane Crystallization

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In a membrane crystallizer, the crystallizing solution is in direct contact with the membrane surface; therefore a solute–membrane interaction will occur in certain circumstances. In this technology, the membrane provides, in the same time, the physical support for mass inter-exchange in vapor phase thus generating supersaturation and the solid support to promote heterogeneous nucleation mechanism. This effect can be due to both the structural and chemical properties of the membrane surface: (1) the porous nature of the surface might supply cavities where solute molecules are physically entrapped leading, locally, to high supersaturation values suitable for nucleation, and (2) the nonspecific and reversible chemical interaction between the membrane and the solute molecules can allow to concentrate and orient molecules on the surface without loss of mobility (Kornberg and Darst 1991), thus facilitating effective interaction proper for crystallization. In the case of complex molecular systems like proteins, the different interaction mechanism is dependent on the patches, with different chemical properties, which are available on the molecular surface.

Hydrophobic and hydrophilic spots, positively and negatively charged functional groups, and hydrogen-bonding moieties are known to provide affinity for almost any kind of non-biological surface. Structural rearrangements of adsorbed molecules develop with solute–surface residence time and are considered as one of the driving forces of adsorption which contributes significantly to nucleation free energy changes (Horbett 1992). Furthermore, the solute–membrane interaction can provide specific solute–solute interaction pathways which would lead to the formation of specific crystal structures (Simone et al. 2006). When inducing heterogeneous nucleation, generally both the induction time and solute concentration necessary for the nucleation decrease, whereas the nucleation density increases on going from a prevalently homogeneous to a prevalently heterogeneous nucleation contribution.

From the classical nucleation approach, the energetic of nucleation concerns mainly the work to create a surface. If there is already a solid substrate in the system, this will decrease the work required to create critical nuclei and will increase locally the probability of nucleation with respect to other locations in the system. The total change in surface free energy will be lowered by favorable interactions between the aggregate and the substrate and unfavorable interactions between the crystallization medium and the substrate, due to the negative value of the second term in the equation above. Consequently, nucleation will be enhanced by increasing the surface area of the substrate. The nucleation work depends on two main parameters: the externally controlled supersaturation ratio and the material surface/solution composition-dependent interfacial energy. Molecules dispersed in solution are first adsorbed on the surface by means of nonspecific attractive interactions. The irregular structure may physically block the lateral migration of the adsorbed protein molecules into the concaves, so that they are forced to be packed into compact aggregates. The trapping of molecules on the surface may result in a relatively higher local supersaturation, which would increase the possibility of nucleation compared with that on an ideally flat

surface. Here, nucleation will follow with the formation of critical clusters comprising molecules forming suitable bond angles with their neighbors, while the molecules in a randomly packed compact structure may form a fractal cluster, which cannot work as a nucleus for crystal growth. Critical clusters then grow into crystals while the fractal clusters grow into larger clusters. This simple mechanism can be generalized to describe heterogeneous nucleation on irregular substrates such as porous surfaces. From a technological point of view, the control of surface porosity in producing membranes can be easily achieved, so that specific membrane nucleants, having the desired value of porosity which might be used to achieve the desired heterogeneous/homogeneous activation Gibbs energy ratio, can be produced.

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Protein Fouling

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In membrane processes, fouling is generally attributed to particulates, colloids, and organic and/or inorganic compounds. Organic compounds could originate from the water source itself (e.g., humic and fulvic substances in surface water) and/or from the microorganisms present in the effluent to be treated (e.g., macromolecules in domestic wastewaters). Within the

macromolecules groups, proteins and carbohydrates have been extensively studied because of their ubiquitous presence in many feed waters treated by membrane technologies. Proteins, in particular, have been observed to significantly impact on the filtration performances in the food and biotechnology industry (van Reis and Zydney 2007) and in the wastewater treatment and recycling (by membrane bioreactors, MBRs, nanofiltration, NF, and reverse osmosis (RO); Wang and Tang 2011).

Proteins are usually present in aqueous solution in a globular/colloidal form (i.e., compact and spherical shape). Their tertiary structure is expected to significantly change with the solution properties (e.g., pH, temperature, salt concentration, presence of other organics). Given their nature (i.e., polymers of amino acid units linked by peptide bonds), proteins present strong affinities with the polymeric surface of the membrane systems, and initial electrostatic interactions can be noticed even before filtration, during passive adsorption tests. Under filtration, the hydrodynamic drag force further increases the tendency of proteins to deposit on the membrane. More details on fouling mechanisms by proteins are available in the article “protein fouling mechanisms.”

While most of the academic studies have focused on pure model protein compounds like bovine serum albumin (BSA), protein fouling in industrial applications is expected to greatly vary in nature and intensity, depending on the type of the feed. For example, porous membranes can be used to concentrate protein solutions in the dairy industry and to filter clean water from activated sludge in MBRs. It is therefore evident that characterization of the relative role of proteins within the formation of the fouling layers remain a complex exercise. In addition, proteinous compounds are expected to denature and/or to aggregate to other materials within the feed matrix. As a result, the respective smaller or larger foulants will lead to different fouling mechanisms, generally difficult to characterize.

Many analyses can be used to measure the relative concentration of proteins in the feed

solution. The conventional Lowry method has been used by default over the years, but the numerous limitations related to this colorimetric test makes it quite unreliable (Drews 2010). Recently, the liquid chromatography-organic carbon detector (LC-OCD) has been used to fractionate the various organic elements within an aqueous sample. Thanks to its complementary organic nitrogen detector (OND), LC-OCD could also provide a quantitative assessment of the level of proteins. Finally, fluorescence techniques like excitation-emission matrix spectroscopy are another emerging tool for protein characterization.

Protein fouling can be easily detected by changes in permeability of the membrane system (i.e., flux decline or transmembrane pressure increase). However, a large number of more advanced characterization techniques have been proposed over the years to identify location and quantity of protein deposition on membranes (Chan and Chen 2004). Scanning electron microscopy (SEM), attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), and confocal microscopy are some of the most commonly used techniques.

Cross-References

► Protein Fouling Mechanisms

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Protein Fouling Mechanisms

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Depending on the membrane systems under investigation, mechanisms for protein fouling will change greatly. Here are concisely reported three major types of protein fouling studied at length in the literature.

Pure Protein Filtration (Lab-Scale Studies)

Over the years, a large number of studies have focused on the characterization of fouling by protein compounds. Bovine serum albumin (BSA) has been generally used as a model macromolecule to mimic the impact of proteins on hydraulic and removal performances in membrane systems. While most of the early work was based on micro- and ultrafiltration (MF and UF), only recent studies have assessed in details the protein fouling mechanisms in nanofiltration (NF) and reverse osmosis (RO). In porous membranes like MF and UF, proteins are expected to adsorb into the polymeric membranes and to gradually block the pores. During long-term filtration, proteins form a cake layer on the membrane surface. Electrostatic interactions between proteins and membrane surface are often cited as the main parameter behind the mechanisms for the initial deposition of proteins occurring in membrane processes, including NF and RO. Severe fouling is generally detected near the isoelectric point of the membrane, for which the electrostatic repulsion forces are minimum. Once the surface of the dense NF/RO membranes is covered by the initial deposition of proteins, fouling mechanisms rely on proteins/protein interactions, and the intrinsic membrane

properties were reported to have insignificant impact during long-term filtration of BSA (Wang and Tang 2011).

Protein Fouling in Food Membrane Processes

Protein is ubiquitously present in many food streams requiring purification, concentration, or treatment by membrane processes. Examples include concentration and fractionation of milk and whey in the dairy industry, production of soy (or other vegetables) protein concentrates and isolates, all generally conducted by MF and UF. For those applications, protein fouling mechanisms are especially studied in order to recommend the most appropriate cleaning strategies to be implemented. As filtration occurs, convection of proteins to the membrane surface results first in concentration polarization, before fouling is detected through the formation of proteinous gel layer. In addition, the constant shear forces implemented as strategy for limiting fouling in those systems generally result in protein surface denaturation and gelation at high concentration. Finally, interaction and aggregation with other compounds (especially divalent ions) are also known to occur, making prediction and modeling of protein fouling very difficult (Li and Chen 2010).

Relative Role of Proteins in Biofouling/Biofilm Formation in Water and Wastewater Treatment

Proteins are also a critical part of the formation of biofouling and biofilm growth in membrane processes. In wastewater treatment and recycling, proteins usually originate from the microorganisms present and growing in the feedwaters. Microbial organisms tend to produce extra cellular polymers (EPS), such as proteins, carbohydrates, and lipids. Once in excess within the boundary of their cell walls, the EPS is then

released in the bulk solution. Both the proteins present around the cells and in a soluble form in the bulk are expected to participate to the formation of biofouling and biofilm on the membrane surface. While biofouling is described as the deposition of organic materials of biological origin (including proteins), further attachment of bacteria and colloidal particles onto the membrane through adhesive forces during filtration is expected to lead to the development of biofilm. As filtration occurs, nutrients and dissolved oxygen are provided to the deposited bacteria and the immobilized bacteria can therefore form the biofilm layer (Marselina et al. 2009).

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Protein Purification by Membrane Operations

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Synonyms

Proteins separation by membrane operations

Membrane systems are used extensively in the purification of high-value proteins from natural sources (e.g., milk and blood plasma) and from the biotechnology industry. This includes the use of normal flow microfiltration for sterile filtration and bioburden reduction, depth filtration for the removal of cell debris and aggregated material, tangential flow microfiltration for initial product recovery, and virus removal filtration (van Reis and Zydney 2007). Ultrafiltration is used for protein concentration and buffer exchange, both for the conditioning of the feed between other unit operations and in the final product formulation. However, actual protein purification, which typically refers to the separation of a desired protein product from other protein impurities, is accomplished using either membrane chromatography or high-performance tangential flow filtration.

Membrane chromatography provides highly selective separations by exploiting differences in protein adsorption/binding interactions, analogous to what is done in column chromatography (Ghosh 2002). The membrane adsorbers used in these systems typically have relatively large pore size with the functional ligands attached to the inner pore surface throughout the membrane. Separations can be accomplished using ion exchange (i.e., charged) ligands, affinity ligands, and hydrophobic interactions. Zeng and Ruckenstein (1999) have reviewed the different base materials and surface modification chemistries that can be used to generate chromatographic membranes.

Transport through membrane adsorbers is typically dominated by the pressure-driven convective flow; diffusional limitations are much less pronounced than in conventional chromatographic beads. This can be particularly important in the purification of large biomolecules and viruses that can have difficulty accessing the internal pore space in chromatographic beads. Membrane adsorbers can be operated at much higher flow rates and with lower pressure drops than conventional chromatography columns, potentially reducing the processing time (Zhou and Tressel 2006).

There has been significant interest in using membrane chromatography for bioprocessing for more than 20 years, but there have been relatively few large-scale commercial installations.

However, recent improvements in membrane materials and chemistries, coupled with a greater appreciation of appropriate target applications, have generated renewed interest in this technology. This is particularly true for flow-through applications in which impurities are bound to the membrane while the product flows directly through the membrane (Zhou and Tressel 2006). This includes the removal of trace DNA, viruses, and endotoxins. Flow-through applications can take full advantage of the high linear velocities possible with membranes. Single-use membrane adsorbers can be very attractive in these applications because of the small amount of impurities that need to be captured. This eliminates the need for reuse studies at small scale and for regeneration and sanitization at large scale, both of which facilitate the development of flexible manufacturing processes (van Reis and Zydney 2007).

High-performance tangential flow filtration (HPTFF) is an emerging technology that uses ultrafiltration membranes for the separation of proteins without limit to their relative size (van Reis and Zydney 2007). This is in sharp contrast to conventional ultrafiltration processes that are generally thought to require a tenfold difference in size between the product and impurity for effective separation. HPTFF has been used to separate monomers from oligomers based on their difference in size, protein variants differing at only a single amino acid residue based on the difference in charge, an antigen-binding fragment from a similar size impurity, and a monoclonal antibody from host cell proteins (van Reis and Zydney 2007).

The high selectivity in HPTFF processes is obtained by exploiting a number of different phenomena. As originally described, HPTFF devices are operated in the pressure-dependent regime at or below the “transition point” in a plot of filtrate flux versus transmembrane pressure. This minimizes membrane fouling and takes advantage of concentration polarization effects to increase performance (Zeman and Zydney, 1996). Further increases in selectivity are obtained by using charged ultrafiltration membranes and by adjusting the solution pH and ionic strength to exploit differences in protein charge between the product and impurity. High degrees of purification

and yield are obtained using a diafiltration process in which the impurities are washed through the membrane and away from the highly retained product. It is also possible to collect the product in the permeate solution with the impurities retained by the membrane.

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Protein Recovery by Membrane Operations

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Protein recovery by membrane operations is synonymous with protein purification by membrane operations and is discussed under that listing.

Protein Separation by Charged UF Membranes

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Charged ultrafiltration membranes can be used to significantly enhance the membrane selectivity,

Protein Separation by Charged UF Membranes, Table 1 Effect of membrane charge and solution pH on the selectivity for separation of albumin and an antigen-binding fragment. Impurity and product refer to the less and more retained proteins, respectively. Thus, selectivity is defined as $S_{\text{albumin}}/S_{\text{Fab}}$ at pH 5 and as $S_{\text{Fab}}/S_{\text{albumin}}$ at pH 8.4

Solution pH	Negative membrane	Positive membrane
5.0	3	120
8.4	200	5

Table adapted from Rohani and Zydney (2010)

making it possible to use these membranes for the separation of similarly sized proteins (Zydney and van Reis 2011). Charged ultrafiltration membranes can provide very high retention of like-charged proteins, enabling uncharged proteins and smaller impurities to be removed in the permeate (Zeman and Zydney 1996). Separations are typically performed at relatively low ionic strength (<10 mM) to enhance the electrostatic exclusion of the charged protein from the charged membrane.

The effect of membrane charge on the separation of bovine serum albumin (MW = 67 kDa, $pI = 4.8$) and an antigen-binding fragment (Fab) from a monoclonal antibody (MW = 45 kDa, $pI = 8.4$) is shown in Table 1. Data were obtained using an unmodified (negatively charged) polyethersulfone membrane and a prototype positively charged membrane. The Fab has a significant positive charge at pH 5, enabling a highly selective separation using the positively charged membrane, with the weakly charged albumin passed into the filtrate. In contrast, albumin has a significant negative charge at pH 8.4, with the negatively charged membrane providing high selectivity with the weakly charged Fab collected in the filtrate. These high selectivities were completely lost when using the membrane with the “wrong” charge at the given pH.

Electrically charged ultrafiltration membranes have been successfully used to separate protein variants differing at only a single amino acid residue, an antigen-binding fragment from *E. coli* host cell proteins, a monoclonal antibody from mammalian cell host proteins, and a model pegylated protein from the unreacted protein and

polyethylene glycol, among others (van Reis and Zydney 2007; Rohani and Zydney 2010).

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Protein Separation by UF

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Membrane processes have been used for bioseparations since well before the start of the modern membrane industry. For example, John D. Ferry’s review article on ultrafiltration in 1936 (Ferry 1936) described the use of membrane technology for enzyme concentration, analysis of bacteriophages and viruses, preparation of cell- and protein-free ultrafiltrates from biological solutions, and sterile filtration, although these systems were limited to analytical-scale processes due to limitations on the available membranes and modules.

There has been considerable interest in using ultrafiltration membranes for actual protein-protein separations, taking advantage of the relatively low cost, high throughput, and easy scalability of membrane systems. Most early efforts at protein separations using ultrafiltration were unsuccessful (Nakatsuka and Michaels 1992), although there were some notable successes in small-scale separations of model protein

systems. Considerable progress in this area has been made over the past 15 years, with specific applications in both the biotechnology industry for the purification of therapeutic proteins and in the fractionation of natural protein sources like whey, egg white, and blood plasma. The key to all of these processes is the development of ultrafiltration membranes/systems with high selectivity between the product of interest and the impurities, where the selectivity is defined as the ratio of the sieving coefficient for the more permeable species to that of the more highly retained species. Selectivities of 100 or greater have been obtained for model systems involving immunoglobulins and albumin, hemoglobin from albumin, lysozyme and albumin, and many others (van Reis and Zydney 2007; Zydney and van Reis 2011).

In most cases, protein separation was accomplished by operating the membrane device at relatively low transmembrane pressures, below the “transition point” as defined by van Reis et al. (1997). High selectivities are obtained by proper choice of both membrane and buffer conditions, with the latter chosen to maximize the difference in electrostatic interactions for the two proteins. For example, positively charged ultrafiltration membranes have been successfully employed for the purification of monoclonal antibodies from mammalian host cell proteins, with the positively charged antibody retained by the charged membrane, while the smaller (and weakly charged) impurities are washed into the filtrate. High yields and purification factors are obtained using a diafiltration mode to increase the removal of impurities.

Protein ultrafiltration has been successfully demonstrated for the purification of antigen-binding fragments (Fab) and monoclonal antibodies from host cell proteins (van Reis and Zydney 2007). Data for monoclonal antibody purification from a harvested cell culture fluid show identical performance, as determined by nonreduced SDS-PAGE and ELISA, for a non-affinity monoclonal antibody purification process using ultrafiltration, in combination with cation and anion exchange chromatography, compared to that of a process using protein A affinity

chromatography for the bulk of the purification (Zydney and van Reis 2011).

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Proteins Separation by Membrane Operations

► Protein Purification by Membrane Operations

Proton-Exchange Membranes for Fuel Cells

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A fuel cell is an electrochemical device that can directly convert the chemical energy of a fuel into electricity. It is regarded as a promising energy conversion approach in the twenty-first century and has received increasing attention worldwide. Among all types of fuel cells, the proton-exchange membrane fuel cell (PEMFC) is considered as the most promising candidate for small stationary power generators and automobiles due to its high

power density, relatively low operating temperature, and fast startup. Compared to inner combustion engines, PEMFCs can reduce pollution (with only water in emission when using hydrogen as fuel), increase energy efficiency (40–50 % for PEMFC vs. 20–35 % for inner combustion), and decrease the nation's dependence on foreign oil (Song 2002).

The proton-exchange membrane is a very important component inside a PEMFC, and its main functions include (a) separation of oxygen from the fuel, (b) conduction of protons, and (c) barrier of electrons. As summarized by Hickner et al., there are six common criteria critical to all high performance PEMs, including (1) high proton conductivity and low electron conductivity, (2) desirable thermal, chemical, oxidative, and hydrolytic stability, (3) desirable mechanical properties in both dry and hydrated states, (4) low permeability to both fuel and the oxidant, (5) low cost, and (6) capability of being fabricated into membrane electrode assemblies (MEAs). Majority of PEM materials rely on absorbed water and its interaction with acid groups for producing proton conductivity. Thus, in most cases, proton conductivities of PEMs increase with the increase of relative humidity (RH) (Hickner et al. 2004).

Dupont's Nafion[®] and other perfluorinated sulfonic acid membranes (e.g., Aciplex[®] from Asahi Kasei, Femion[®] from Asahi Glass, PRIMEA[®] Series of MEAs from W.L. Gore & Associates, etc.) are currently popular to use for low temperature (<100 °C) PEMFCs due to their high proton conductivity, desirable mechanical strength, and good chemical stability. However, some disadvantages, such as high cost and high dependence of proton conduction on the water content, seriously limit the industrial application of these membranes. It is desirable for a PEMFC to operate at high temperatures and low RHs since high-temperature operations can accelerate the reaction rates at the anode/cathode and increase the anode's tolerable level of CO in the fuel, and low humidity operations can facilitate the water management of the fuel cell system. The US Department of Energy has established a goal of 0.1 S/cm for the proton conductivity of the PEM, with target operating conditions at 120 °C and 50 % RH (Hickner et al. 2004).

Cost-effective and thermally stable alternative membranes, including sulfonated polyimide (SPI), sulfonated poly(arylene ether sulfone) (SPAES), sulfonated poly(aryl ether ketone) (SPAEEK), and polybenzimidazole (PBI)-based membranes, etc., have drawn interests in the past decade. SPI, SPAES, and SPAEEK copolymers are synthesized by copolymerization of sulfonated monomers (Hickner et al. 2004). These sulfonated copolymer-based membranes are still highly dependent on water content, and a hydrophilic component has been incorporated into the membrane for water retention (Bai and Ho 2011). But, the oxidative and hydrolytic stability of these copolymers needs to be further improved prior to long-term operations. On the other hand, H₃PO₄-doping has been identified as a successful approach for the application of PBI as high-temperature and low humidity PEMs (Li et al. 2009; Bai and Ho 2011). In this case, fuel humidification is not necessary in fuel cell operations due to the unique proton conduction mechanism by self-ionization and self-dehydration of H₃PO₄. In addition, the PBI polymer showed very desirable stability under fuel cell operations, even at high-temperature (>150 °C) conditions. However, acid leakage through such membranes during long-term fuel cell operations remains to be a concern. Significant research efforts are continuing in both academia and industry for the further improvement/development of perfluorinated, alternative hydrocarbon polymer-based and polymer/inorganic hybrid PEMs.

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Pulp and Paper Industry and Membrane Operations

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Synonyms

Paper industry and membrane operations; Pulp industry and membrane operations

Membrane technology has adapted to pulp and paper mill applications with the aim of decreasing water consumption, recovering and recycling valuable compounds, and reducing the environmental impact of the mills. Today (2013), the most common membrane application in the pulp and paper industry is coating color recovery from waste coating streams by ultrafiltration. Membrane technology is also used in the treatment of a wide variety of process streams and effluents. Depending on the application, the treatment is performed either with pressure-driven membrane filtration processes (micro-, ultra-, or nanofiltration or reverse osmosis) or with membrane bioreactors (MBR) (Mänttari and Nyström 2009; Nuortila-Jokinen et al. 2003).

Pulp and paper mill process streams and effluents form a heterogeneous group of waters, because every pulp and papermaking process has its special characteristics, which also affects its process and wastewater quality. Thus, every pulp or paper mill has different water and effluent qualities. Moreover, the primary motives for the use of membrane filtration vary depending on the production processes at the mill and local legislation, and therefore, every reuse application has specific quality criteria. For these reasons, it is not really possible to specify in details which membrane is the most feasible for pulp and paper applications or to set common quality requirements for process streams produced by membranes (Mänttari and Nyström 2009; Nuortila-Jokinen et al. 2003).

Pulp and paper mill process streams and effluents are very complex mixtures of compounds originating from the raw materials and from different chemicals. They contain wood-based compounds, such as polysaccharides, lignin and wood extractives and degradation products of the wood component, and, depending on their origin, chemicals or additives used in the processing of raw materials or in the manufacturing of the end products. When a complex mixture of this kind is treated, fouling can significantly be diminished by a feasible membrane choice. Usually, less fouling occurs when a hydrophilic membrane, which carries only a weak charge, is used (Mänttari and Nyström 2009; Nuortila-Jokinen et al. 2003).

Today (2013) pulp and paper mill processes are mainly water based. Tolerance to solvents is only seldom a significant factor in membrane choice. Requirements for the chemical stability of the membranes depend on the application. pH of the process streams and effluents varies depending on their origin from below 2 to 14 and some effluents contain oxidizers. Also temperature of the streams and effluents varies depending on their origin. Temperature can be close to 10 °C (effluent from the external water treatment) or higher than 100 °C (some process streams at pulp plants). Membranes might also be exposed to microorganisms capable of degrading membranes manufactured from cellulose-based materials (Mänttari and Nyström 2009; Nuortila-Jokinen et al. 2003).

Pulp and paper mill process streams and effluents contain fibers and other suspended solids. They have also high contents of colloidal material. Due to this, a comprehensive pretreatment is needed, when modules with high packing density are used (e.g., spiral wound modules widely used in water treatment). Another specific characteristic of pulp and paper mill applications is that the volumes of the streams needed to be treated are huge and extremely high membrane filtration capacities are demanded. High shear rate membrane modules can produce the high capacities and usually also tolerate the solids and high content of colloidal material in the feed stream. The high shear rate modules currently used in pulp and paper mill applications are typically tubular

modules or modified plate and frame constructions, for instance, the cross-rotational (CR) module (Metso Paper), in which the shear rate is generated by rotors near the membrane surface (Mänttari and Nyström 2009; Nuortila-Jokinen et al. 2003).

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Pulp Industry and Membrane Operations

► Pulp and Paper Industry and Membrane Operations

Purification of Plasma from Cholesterol by Immunoaffinity Membranes

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Coronary heart diseases are responsible for the 4.3 million deaths in all of Europe and also can cause lifetime disability. The annual economic cost is estimated to be 192 billion with a substantial increase (Harland 2012). Together with the high blood pressure, LDL cholesterol is widely recognized as one of the major risk factors in the development of coronary heart diseases because of its ability to build up in the lining of arteries to form

atheromas and fatty acid deposits (Bruckert 1999; Thompson 2003). In the case where dietary and drug therapy is insufficient to set safe blood cholesterol level, extracorporeal cholesterol removal techniques with different selectivity and specificity have been used. Plasmapheresis, cascade filtration, heparin induced LDL precipitation (HELP), thermofiltration, dextran induced LDL precipitation, and direct adsorption of lipoproteins are the examples (Blaha 2003). The most selective removal of LDL has been achieved by the use of monoclonal antibodies against the apoB100, the main protein component of LDL, as a ligand (Kane et al. 1975). This allows removal of harmful LDL without decreasing useful HDL and other plasma proteins. Conventional gel-bead columns have certain limitations especially when studying with viscous media such as human blood. Alternative carriers such as membranes, monoliths, and cryogels are designed to solve drawbacks of gel-beads such as high-pressure drop and flow rate limitations that limit efficiency of applications (Berele et al. 2011). In random immobilization of antibodies, they can bind to the polymer surface at many different points (Denizli 2002; Yavuz and Denizli 2003, 2005). This generally results in decrease in the antigen-binding capacity because the accessibility of the antigen-binding sites is prevented in most cases. Anti-LDL immobilization onto the polymeric carriers can be performed in an oriented mode to leave its antigen-binding fragments free. It can be done by either using Fc receptor proteins such as Protein A and Protein G, by using carbohydrate binding polymer in order to bind through the carbohydrate moiety, or by using artificial or digestion product Fab fragments. Immunoaffinity adsorbent obtained by oriented immobilization of anti-LDL onto the biocompatible PHEMA cryogel membranes show better LDL adsorption capacity (129 mg LDL/g) from hypercholesterolemic human plasma than random anti-LDL immobilized adsorbent (111 mg LDL/g) while the amount of anti-LDL bound in an oriented mode was the one third of the random immobilized. Nonspecific adsorption of other lipoproteins was very low in both cases. It has been also shown that these adsorbents can be

used many times without significant decrease in the adsorption capacity (Bereli et al. 2011).

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PVA-Based Anion-Exchange Membranes

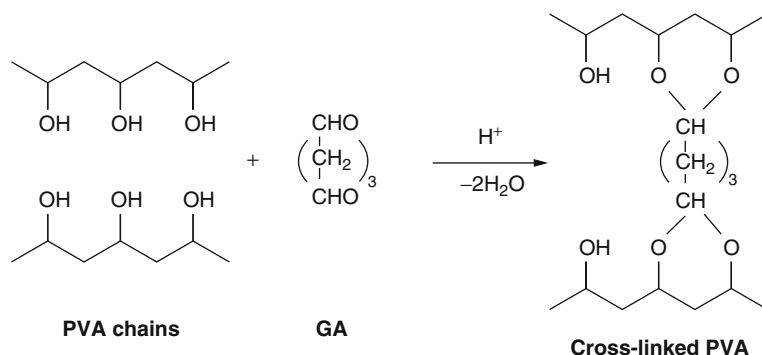
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PVA-based anion-exchange membrane consists of poly(vinyl alcohol)(PVA) matrix and anion-exchange groups (positively charged groups); hence, anions selectively permeate through the membrane. PVA is one of the most popular polymers that has been used as a membrane matrix, because a film made from PVA shows good physical properties, high hydrophilicity, process ability, biocompatibility, and good chemical resistance.

PVA is a water-soluble polymer and does not have any anion-exchange groups. Hence, a PVA-based homogenous anion-exchange membrane (AEM) can be prepared easily by casting an aqueous solution of mixed PVA and polycations and then cross-linked PVA polymer chains. PVA is a semicrystalline polymer; thus, heat-treatment above the glass-transition temperature increases the crystallinity of the polymer, which acts as a physical cross-linking. PVA chains can also be chemically cross-linked using cross-linking agents such as glutaraldehyde(GA) as shown in Fig. 1. Hence, the degree of swelling of a PVA-based AEM, which plays an important role in its permselectivity for anions and membrane resistance, can be easily controlled by varying the annealing and/or chemical cross-linking conditions. The AEM thus obtained has a semi-interpenetrating network (semi-IPN) structure in which polycation chains are immobilized in the polymer cross-linked network matrix. The ion-exchange capacity of such membranes can be easily controlled by changing the polymer ratio of PVA to polycations. AEMs with a semi-IPN structure have been prepared by blending PVA and a polycation such as poly(acrylamide-co-diallyldimethylammoniumchloride), poly(allyl amine), etc. However, those electrodialytic transport properties are not enough to compete with commercially available homogeneous AEMs. An additional disadvantage of AEMs with semi-IPN structure is low long-term stability when immersed in solution due to the dissolution of uncross-linked water-soluble polyelectrolytes in the network into the solution. To avoid the problem of dissolution of uncross-linked water-soluble polycations, AEMs with IPN structure were prepared by blending PVA and a PVA-based copolymer-type polycation, such as poly(vinyl alcohol-co-methacryloyl aminopropyl trimethyl ammonium chloride) (Fig. 2). ED processes with PVA-based AEMs have potential applications to many industrial fields such as water treatment, food industry, medical supplies, acid recovery from pickling solution, wastewater treatment, etc. The AEMs will also be potentially applicable to polymer electrolytes for alkaline direct methanol fuel cells because the AEMs have low methanol crossover.

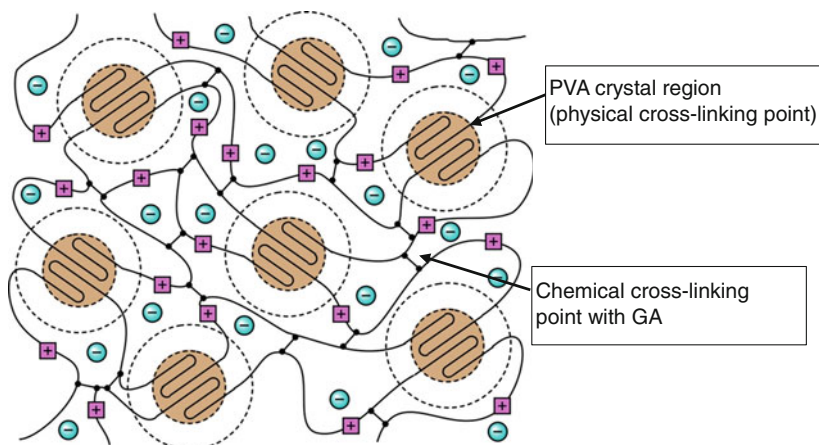
PVA-Based Anion-Exchange Membranes,

Fig. 1 Scheme of chemical cross-linking of poly(vinyl alcohol) (PVA) using glutaraldehyde (GA) (Higa et al. 2012)



PVA-Based Anion-Exchange Membranes,

Fig. 2 Schematic diagram of membrane structure of an AEM with IPN structure



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Q

Quantitative Structure-Property Relationships (QSPR)

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QSPR models can be defined as empirical equations, used for estimating various physical or thermodynamic properties of molecules. A QSPR model can be described as follows:

$$P = a + b \cdot D_1 + c \cdot D_2 + d \cdot D_3 + \dots,$$

where P is the physical property of interest; terms $a, b, c, \dots$ are regression coefficients, and $D_1, D_2, D_3, \dots$ are parameters derived from the molecular structure, also referred to as descriptors. A variety of different types of descriptors can be used. The simplest types are constitutional or topological descriptors, such as the number of carbon atoms, and parameters describing types and order of the chemical bonds in the molecules. Various geometrical descriptors, including the principal moment of inertia, can also be used. The most important and also the most complicated descriptors are electrostatic and quantum chemical descriptors. The electrostatic descriptors are parameters which depend on the charge distribution within the molecule, including the dipole moment. An example of a quantum chemically derived

descriptor is the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies (Dyckjær and Jóónsdóttir 2004).

The QSPR approach has been growing up in the field of drug design. In this field common approaches such as QSPR as well as quantitative structure-activity relationship (QSAR) are used. Application in other fields, such as QSPR, to model various physical properties of carbohydrates (Dyckjær and Jóónsdóttir 2004) and the development of QSPR models for the prediction of skin permeability (Neely et al. 2009) have been reported in literature. An interesting application linked with membrane processes is the development of QSPR models that consider the simultaneous correlation of organic solute rejection with multiple molecular parameters for RO membranes, with the potential for being applied to a broad range of compound classes (Libotean et al. 2008).

The development of QSPR model involves several steps: collection and preparation of data $\rightarrow$ molecular optimization and generation of descriptors $\rightarrow$ selection of descriptors $\rightarrow$ QSPR model building $\rightarrow$ model validation. Descriptor data can be obtained from literature, performing experiments, or calculations by using commercial software (e.g., Codessa software package) as well. Techniques such as PCA, genetic algorithms (GAs), and stepwise regression have been widely used to select optimal subset of descriptors. Linear and nonlinear models can be applied for

developing QSPR models. The nonlinear models were mainly developed based on artificial neural networks (ANNs) (Khajeh and Modarress 2013).

QSPR/QSAR models should be associated with appropriate measures of goodness of fit, robustness, and predictively, according with the guidelines proposed by the Organisation for Economic Co-operation and Development (OECD). In this sense, the assessment of QSPR models is established using statistical validation procedures which consist of measuring both internal model performance (goodness of fit and robustness) and external performance (predictively). In particular, the model performance should be evaluated with respect to the absolute and relative absolute average errors and standard deviation of the errors. Internal model validation is based on the leave-one-out procedure (LOO) cross-validation approach.

Despite the potential and power of this approach, applications in membrane technology are not so common yet.

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R

Radiation-Induced Grafting

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Grafting initiated by radiation technique is known as radiation-induced grafting or radiation-induced graft polymerization (see article graft polymerization). Radiation acts as an initiator in the grafting process which generates controlled concentrations of active sites, depending upon the irradiation type, rate, and dose, which are distributed almost evenly throughout the entire volume of the sample and initiate polymerization. Owing to high energy, radiation makes it possible to carry out the process in the solid or viscous state at substantially lower temperatures than in the case of traditional, chemical initiators.

Types of Radiation

A variety of high-energy radiations can be used for the grafting process (Heger 1990). This may include electromagnetic radiation, such as x-rays and gamma rays, or charged particles, such as beta particles and electrons. The commonly used gamma radiation source is CO^{60} which has a

long half-life of 5.3 years and emits radiation of 1.17 and 1.33 MeV (mean value of 1.25 MeV).

Methods of Radiation Grafting

Radiation-induced grafting could be proceeded by simultaneous irradiation or pre-irradiation technique.

In the case of the simultaneous irradiation method, the polymer is irradiated in the presence of a monomer under inert atmosphere. Since all the components of the system exposed equally to the radiation, it radiolyzed nonselectively. This process has impact on the kinetics of polymerization, and as a result, the extent of homopolymerization is always high in simultaneous radiation grafting. The pre-irradiation method, on the other hand, involves the activation of the base polymer prior to the grafting reaction. As a result, considerable structural changes take place during the irradiation of the polymer itself, which have their impact on the physical properties of the resultant membrane. During pre-irradiation, the radicals generated on the polymer chains and the radical at one chain may either combine with another radical from the adjacent chain leading to the cross-linking or undergo chain scission, thereby producing terminal unsaturation. The scission and cross-linking process also depends

upon the nature of polymer to be irradiated (Sherazi et al. 2008; Gupta et al. 2004).

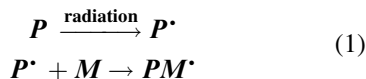
Radiation-Induced Grafting Mechanism

The irradiation of polymers may cause homolytic fission and thus generates free radicals on the polymer. Since radiation is generating the radicals for subsequent grafting, thus the presence of any other initiator is not essential. The medium of irradiation is important which affects the grafting mechanism. If the irradiation is performed in an inert atmosphere, then radicals are formed, but if air or oxygen is present, then peroxides may be formed on the polymer. The lifetime of the free radical depends upon the nature of the backbone polymer.

The mechanism for pre-irradiation grafting and simultaneous grafting are as below:

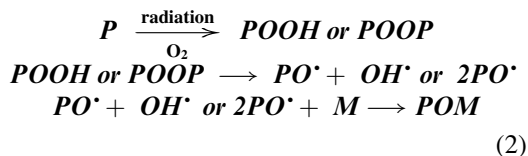
Pre-irradiation Grafting (In an Inert Atmosphere)

As already described in the pre-irradiation technique, the polymer backbone is first irradiated in vacuum or in the presence of an inert gas to form free radicals. The irradiated polymer substrate is then treated with the monomer, in liquid or vapor state or as a solution in a suitable solvent.



Pre-irradiation Grafting (In the Presence of Air/Oxygen)

If irradiation performed in the presence of air or oxygen, hydroperoxides or diperoxides will be formed, depending on the nature of the polymeric backbone and the irradiation conditions. When the grafting has to be performed, these stable peroxy products are treated with the monomer at higher temperature. The peroxides undergo decomposition to radicals, which then initiate grafting.

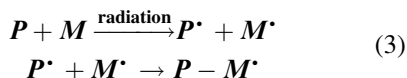


Peroxy products have the advantage that these can be stored for long periods before performing the grafting step.

Simultaneous Irradiation Grafting

In the case of simultaneous irradiation technique, the polymer and the monomers are irradiated simultaneously, to form free radicals and subsequent addition.

Since the monomers are also exposed to radiation in this technique, thus homopolymer formation also takes place. The simple representation of the process is as below.



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RAFT Chemistry

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RAFT chemistry is one of the most important preparation methods to synthesize high-

of the technology toward a commercialization stage. One solution found is to firmly bond the photocatalysts to the surface of the membrane, via a RAFT polymer incorporating chelating groups. For example, TiO_2 has been immobilized onto polypropylene membranes, thanks to the surface-initiated RAFT polymerization of acrylic acid (Yang et al. 2011). The same approach of surface-initiated RAFT polymerization has been explored to add new functionalities to the filtration membrane. Zwitterionic polysulfobetaine brushes have been produced on the top of a cellulose membrane for improving hemocompatibility and antifouling property (Yuan et al. 2013). Pore size tuning could also be achieved via RAFT chemistry by an initiation of the polymerization from the pore walls. The RAFT process is here required to highly control the polymer chain length and thus the pore size decreases. For example, a track-etched poly(vinylidene fluoride) membrane has been treated to functionalize its pore size as well as to decrease it via the RAFT polymerization of acrylic acid (Barsbay et al. 2013).

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Reactive Air Brazing (RAB) for Gas Separation Membranes

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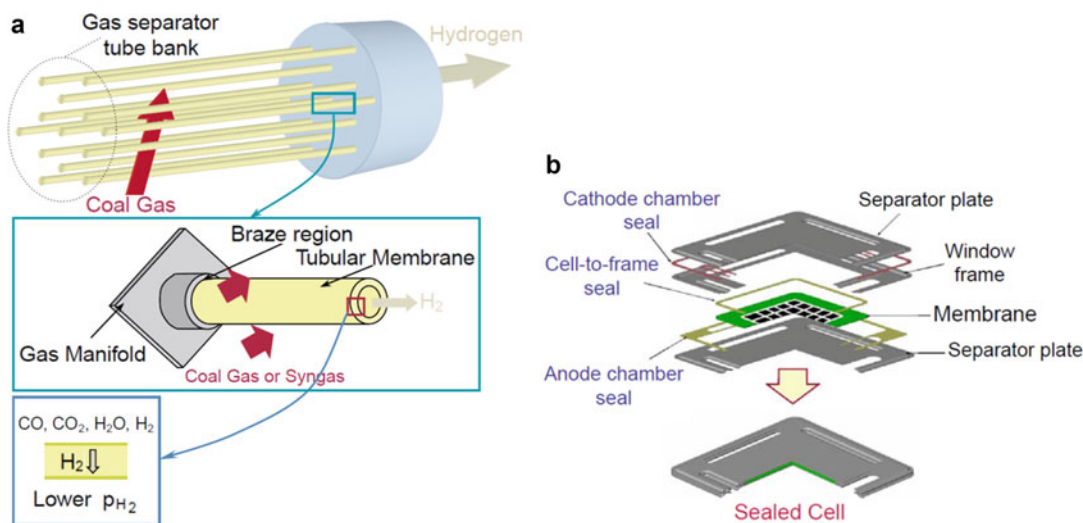
Introduction

Reactive air brazing (RAB) is a technique that has been developed in the last 10 years for high-temperature joining purposes as an alternative to widely used glass or glass-ceramic sealants and other high-temperature joining techniques that were often found to be less reliable and suitable (such as diffusion bonding, reaction bonding, active metal brazing, or brazing of metallized ceramics) (Nicholas and Mortimer 1985; Chung and Iseki 1991; Kim et al. 2005a).

The RAB concept (see Fig. 1) holds the promise of providing durable, robust, heat-resistant, and gas-tight seals for ceramic-to-metal and ceramic-to-ceramic components of power generation ceramic membrane systems (mixed ionic-electronic conducting (MIEC) membranes for high-temperature hydrogen or oxygen separation) and various process applications (such as the coal-based integrated gasification combined cycle, IGCC) as well as solid-state electrochemical devices (such as solid oxide fuel cells (SOFCs) fuel gas reformers and electrochemical sensors) (Weil et al. 2005a, 2006a).

Method

RAB emerged as a technique for joining dissimilar materials (both in terms of their thermal



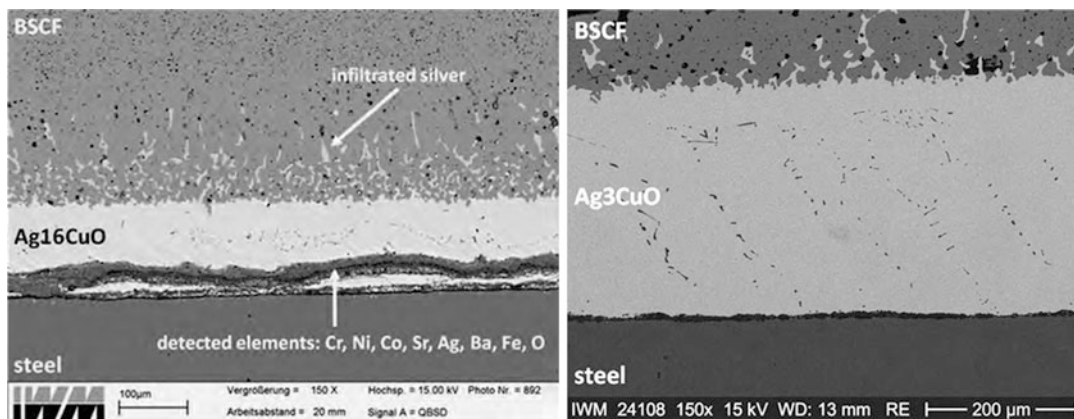
Reactive Air Brazing (RAB) for Gas Separation Membranes, Fig. 1 Schematic illustrations of the high-temperature applications of RAB sealing for: (a) large-scale membrane-based gas separation systems (either for oxygen or hydrogen separation; shown here is a hydrogen

separation membrane) and (b) planar SOFC stacks composed of interleaved layers of sealed ceramic membranes and metal interconnects (Reproduced from Weil et al. (2006a) with permission from Elsevier)

expansion coefficients and chemical stability) by utilizing a brazing alloy system made from a metal oxide (partially or fully) dissolved in a noble metal filler. When heated to the melting point (greater than the operating temperature of the ceramic-metal unit) the binary RAB braze under capillary forces fills the space between the two joining components, while the metal oxide content reactively modifies one or both faying surfaces (without degradation). Upon cooling a seal is formed that remains hermetic, mechanically strong and chemically resistant at operating temperatures (or at room temperature). The RAB process is readily performed in air without the need for a naked flame, fluxing agents, vacuum, or reducing gas atmospheres (Weil et al. 2003, 2005b). Typical RAB systems investigated include Ag-Cu_xO, Ag-V₂O₅, Ag-MoO₃, and Pt-Nb₂O₃ among which Ag-CuO is one of the most promising and best-studied RAB braze systems for MIEC oxide-based membranes (Weil et al. 2006b).

Examples, Challenges, and Prospects

Weil et al., pioneers in the RAB technology for MIEC-based device technology, carried out a series of wettability experiments by the sessile drop technique (contact angle measurements) to determine the effect of the addition of different CuO compositions on the wetting behavior of the noble metal on La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF6428) and preoxidized FeCrAlloy substrates, two prototype materials for the (MIEC) ceramic-to-metal joining system. Following from the results of these experiments and subsequent microstructural and chemical analyses of the braze-substrate interfaces, Weil et al. conducted joining experiments using the braze compositions that exhibited the best wetting, namely Ag-2 mol % CuO and Ag-4 mol% CuO brazes heated to 1100 °C (Weil and Hardy 2002). Later studies by Hardy et al. on Ag-CuO/LSCF6428 joints, that were formed with compositions of CuO in a range of 1.4–16 mol%, demonstrated the efficacy of



Reactive Air Brazing (RAB) for Gas Separation Membranes, Fig. 2 Scanning electron microscope (SEM) comparison of braze-substrate interfaces of two BSCF-

steel joints brazed at 1050 °C using Ag – 16 mol% CuO and Ag – 3 mol% CuO fillers (Reproduced from Kaletsch et al. (2012b) with permission from ASM International)

RAB, optimal braze wettability, joint ductility, and resulting flexural strengths greater than 100 MPa (Hardy et al. 2004). In comparison, Kim et al. reported a maximum average strength of 221 MPa for Ag-CuO brazed polycrystalline alumina joints with a CuO content of 8 mol% (Kim et al. 2005a). Similarly, for yttria stabilized zirconia (YSZ) substrates and Ag-CuO brazes, the authors showed that with increasing CuO content of up to 8 mol%, both the wettability of the braze and the bending strength of the brazed YSZ joint increased (Kim et al. 2005b).

A recent study conducted by Kaletsch et al., looked into the effects of different Ag-CuO compositions on brazing $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582) and austenitic steel (AISI 314) at 955–970 °C. Higher CuO content results in better wetting but appears to affect the local chemistry and microstructure of the interfacial regions of the brazed joints (see Fig. 2) resulting in poorer mechanical strength and porosity and inadequate seals and leaks. By contrast, the low CuO content filler (Ag-3 mol% CuO) in the BSCF5582-steel specimens did not promote the growth of the reaction layers at the interface with the braze, not even after annealing in air at 850 °C for 300 h (Kaletsch et al. 2012a, b). The latest results by Chen et al. highlight the engineering challenges ahead to ensure high-integrity RAB joints for oxygen transport membranes (OTM) with high

fluxes (such as $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$) integrated in high-temperature membrane-based applications such as emission-free coal-fired power plants (Chen et al. 2015).

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Reclaimed Water, Membranes for

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The recovery, or reuse, of effluents from municipal wastewater treatment plants (MWWTPs),

commonly called municipal wastewater reclamation, represents a viable alternative to water shortage and contributes to an integral sustainable water management. This is an important alternative water source for many regions. There are no universal water quality standards defined for the reclaimed water, but health hazard is the main issue always mentioned within all available legislations (EPA and AID 2004; EPHC et al. 2006; EU 2000; OAL 1978, amended in 1998; Winpenny et al. 2010). The most viable treatment train for these effluents depends mainly on the final water use, considering its risks and constraints (Table 1), and the particular permit requirements. Additionally, it also depends on the level of water stress and availability, the geographical situation, the stakeholders' acceptance, and the economic figures.

Each reclamation case is defined by the final water use that must be directly connected to its specific treatment. The removal efficiencies that may be achieved after applying different technological alternatives, to reclaim municipal wastewater, are summarized in Table 2 (Asano et al. 2007; Ordóñez et al. 2014, 2011).

Conventional tertiary treatment (typically, flocculation + clarification + filtration + disinfection) is usually applied when reclaimed water would just be used for less strict uses, as agricultural irrigation, whereas membrane filtration is required for more exigent uses to avoid any health hazard or risk. In this framework, the main processes used for the retention of microbial and suspended solids are microfiltration (MF) and

R

Reclaimed Water, Membranes for, Table 1 Risks and constraints of the different sectors using reclaimed water (Adapted from Bixio et al. (2008))

Agriculture	Urban	Industrial	Environmental
Pathogens Soil, water, atmospheric pollution (salinity, toxicity, eutrophication, etc.) Product quality Emerging contaminants	Pathogens Microbial growth (slime/scale formation) Foaming Corrosion Deposition/clogging Staining Hazards to possible cross-connection with potable water supply	Pathogens Microbial growth (slime/scale formation) Foaming Corrosion Deposition/clogging Staining Hazards to possible cross-connection with potable water supply Product quality	Pathogens Soil, water, atmospheric pollution (salinity, toxicity, eutrophication, etc.) Emerging contaminants

Reclaimed Water, Membranes for, Table 2 Removal efficiencies (%) of different treatments applied to reclaim municipal effluents (Adapted from Ordóñez et al. (2014))

Parameter	CAS ^a	CAS + filtration	CAS +BNR ^b	CAS +BNR + filtration	MBR	MBR +IE	CAS +MF/UF +RO MBR+RO
TSS, mg/L	96–94	98	95–96	99	>98	>98	>99
TDS, mg/L	0	0–19	0–19	0–19	0–19	–	85–98
VOCs, µm	90	90	90–95	90–95	90–95	90–95	>99
COD, mg/L	84–90	88–91	92–95	92–96	>96	>96	96–99
BOD ₅ , mg/L	93–95	94–95	95–96	98–99	>99	>99	>99
TOC, mg/L	85–88	88–90	90–92	98–99	>98	>98	99.0–99.9
Total nitrogen, mg/L	25–50	25–50	85–89	90–93	>86 ^c	>80	>95
Total phosphorous, mg/L	0–17	0–33	75–83	>83	58–93 ^d	>80	>86
Metals, mg/L	33–40	33–40	33–40	33–40	Trace	Trace	–
Total coliforms, CFU/100 mL	99.0–99.9	>99.9	99.0–99.9	99.0–99.9	>99.9	>99.9	~100
Protozoan cysts and oocysts, CFU/100 mL	0–99.9	>99.9	>99.9	>99.9	>99.9	>99.9	~100
Viruses, PFU/100 mL	0–90.0	0–99.9	0–90.0	0–90.0	>90	>90	~100

^aCAS: conventional activated sludge + nitrification^bBNR: biological nutrient (N and P) removal^cWith anoxic stage^dWith coagulant addition

ultrafiltration (UF) (Judd and Jefferson 2005). These treatments produce water for environmental or industrial uses, as cooling water, or they are applied as pretreatments for nanofiltration (NF) or reverse osmosis (RO), which are required to generate water of very high quality, even drinking water, as in Singapore (Wang et al. 2008).

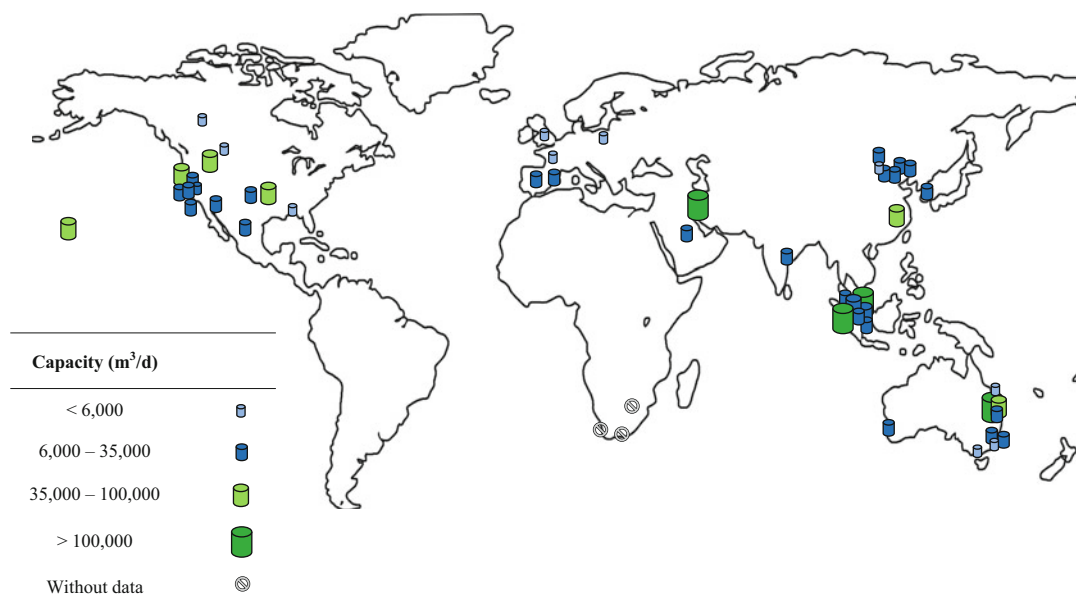
Although almost any membrane design can be applied for the treatment of wastewater with low suspended solid content, only specifically designed membranes and operation modes would be able to handle effluents carrying high amounts of solids, bacteria, or organic pollutants, very frequent in effluents from MWWTPs. In these cases, higher cross-flow velocities or submerged systems may be a good option, including membrane bioreactors (MBRs) (Judd 2006; Ordóñez et al. 2014).

Regarding the current implementation of this technology, the main world cores are Australia, Asia (Singapore and China), and the USA, mainly used for aquifer recharge, potable use, and industrial applications (Fig. 1).

Main Challenges: Fouling and Reject Stream Management

In general, dissolved organic matter typically present in effluents from MWWTPs (TOC $\approx$ 5–20 mg/L; BOD₅ $\approx$ 3–10 mg/L), together with other colloidal matter, may produce fouling. Furthermore, although salinity of these effluents is much lower than seawater ($\approx$ 1,500 versus 38,000 mg/L, respectively), scaling may be produced, moreover if the MWWTP receives a large amount of industrial wastewater (Ordóñez et al. 2011). In this case, special attention must be given to the industrial cleaning processes that may produce periods in the MWWTP in which the residual chemicals create membrane fouling.

To minimize fouling problems, membrane surface may be modified to further enhance their antifouling behavior (Judd and Jefferson 2005). Another strategy is the installation of aeration devices, mainly in MF and UF systems, to enhance surface membrane shear, but it highly increases the cost (Judd 2006). The selection of



Reclaimed Water, Membranes for, Fig. 1 Worldwide distribution of the main municipal water reclamation facilities reclaiming water through membrane processes (Adapted from Ordóñez et al. (2014))

the best cleaning strategy (type of chemical, cleaning conditions, and frequency) for backwash and cleaning-in-place (CIP) is the key to achieve both a constant membrane system performance and the lowest possible contribution to operational cost (Caothien et al. 2003).

Another significant problem is the production of concentrated streams. Different initiatives regarding the removal of hazardous components from concentrated streams have been reported, but although some compounds are removed, others equally dangerous remain. Special attention will be given in the future to the accumulation of emerging contaminants. The best management alternative for these streams would be finding direct applications for them, namely, recycle them.

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Recovery of Antibiotics from Fermentation Broth Membrane Operations

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The first step in the recovery of antibiotics from fermentation broths is the separation of the cells from the liquid growth media. However, the purification process is different whether or not the product is intracellular or extracellular. In antibiotic production, either options are possible even if the majority of antibiotics, including penicillins, cephalosporins, and streptomycin, are extracellular products. When the desired product is intracellular, after a coarse liquid removal step, the cells are lysed to release the product. The clarification of the antibiotic is then performed to remove the cell debris. In both cases, since the antibiotics are relatively small molecules, a concentrate containing the solid biomass and a permeate containing the antibiotic and other impurities are obtained (Brites Alves et al. 2002).

The important steps of the antibiotic production process are the separation of mycelial cells, the chemical extraction of the active molecule, and the purification and crystallization of the target antibiotic (Lipnizki 2010). Cell harvest is generally carried out by rotary vacuum filters or by centrifugation, but, apart from the high energy consumption, with these techniques a complete

recovery is not possible since a large quantity of the antibiotic is entrapped in the solid cake. To increase the recovery, an extensive cake washing is required which entails further energetic costs. Membrane cross-flow filtration with ceramic membranes, or hollow fibers, is achieving widespread application as an alternative to conventional filtration and centrifugation, due to their low-energy requirements (Adikane et al. 1999). Moreover, the use of membranes permits the introduction of a diafiltration step to improve upon the yield of antibiotic recovery, without additional investment costs.

Microfiltration and ultrafiltration are feasible options, but the use of ultrafiltration is preferred since it retains also some surface-active components, such as proteins and polysaccharides, present in the fermentation broths which are responsible for emulsion formation. These emulsions are a severe problem in the subsequent extraction step since they may lead to product contamination, low extraction yields, high solvent losses in the extracted broth, and clogging of pumps or other separation equipment. The use of ultrafiltration, with an appropriate molecular weight cutoff (MWCO), retains the components responsible for emulsion formation and eliminates the need of anti-emulsion products, which can also cause an environmental pollution problem since chemical synthetic surfactants are difficult to degrade (Tessiera et al. 2005). The practice showed that ultrafiltration is an efficient technique for the recovery of antibiotics from fermentation broths. Ultrafiltration could significantly improve the extraction operation in terms of phase separation, elimination of the need for any de-emulsifier or wet agent, and increase extraction recovery and product quality (Koltuniewicz 2010).

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Recovery of Polyphenols from Olive Mill Wastewaters by Membrane Operations

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Olives contain an appreciable amount of bioactive compounds such as polyphenols with remarkable health benefits. They are potent antioxidants and exhibit various other physiological activities including antiinflammatory, antimicrobial, antiallergic, anticarcinogenic, and antihypertensive activities (Obied et al. 2005).

The biophenolic fraction of olive oil comprises only 1–2 % of the total phenolic content of the fruits; the remaining 53 % and 45 % are lost in olive mill wastewaters (OMWs) and the olive cake, respectively. Typical biophenols occurring in OMWs are benzoic acid derivatives (4-hydroxybenzoic, protocatechuic, vanillic acids), hydroxycinnamic acid derivatives (ferulic, caffeic acids), tyrosol, homovanillyl alcohol, hydroxytyrosol, and oleuropein. These compounds represent a precious resource of potentially useful chemical substances (after their direct recovery or chemical transformation) for cosmetic and pharmaceutical industries and in food processing and food product conservation.

Several techniques have been proposed individually or in integrated forms to recover phenolic compounds from OMWs including solvent

extraction, supercritical fluid extraction, and chromatographic separation.

Membrane operations such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), mostly in sequential form, represent useful technologies for the recovery, purification, and concentration of polyphenols with regard to their molecular weight cutoff values. They offer significant advantages over conventional methodologies in terms of low energy consumption, no additive requirements, and no phase change.

Integrated membrane processes based on the use of these operations permit to obtain purified water which can be discharged in aquatic systems according to national regulations or to be used for irrigation. NF is typically employed for the separation of most part of phenolic compounds (Paraskeva et al. 2007).

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Recovery of Polyphenols from Wine Wastewaters by Membrane Operations

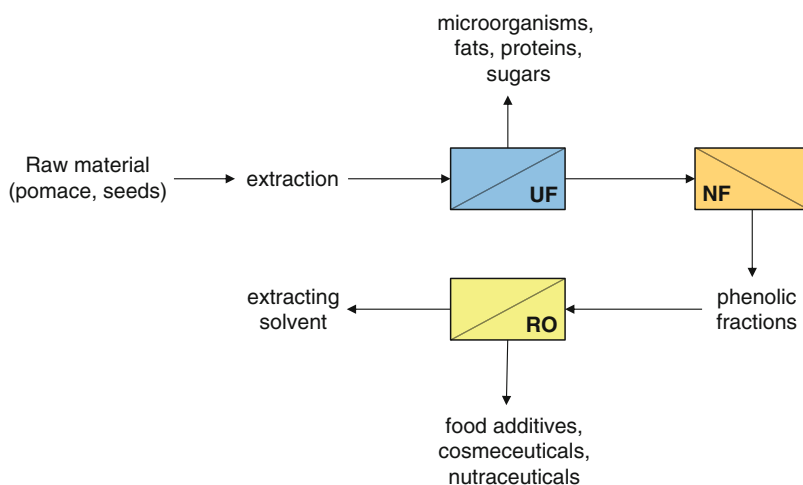
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Grape seeds and pomace (a solid material consisting of skins and grape seeds) are typical by-products of the winemaking process containing phenolic compounds.

Recovery of Polyphenols from Wine Wastewaters by Membrane Operations,

Fig. 1 Purification, fractionation, and concentration of polyphenols from wine wastewaters by integrated membrane process



Grape seeds contain basically (w/w) 40 % fiber, 16 % essential oil, 11 % protein, 7 % complex phenolic compounds, sugars, minerals, and other substances (Campos et al. 2008). Grape skin is a source of anthocyanidins and anthocyanins, natural pigments with antioxidant properties.

These phenolic compounds have an extremely high market value as food additives, nutraceuticals, and cosmeceuticals, due to their biological activity (Crespo and Brazinha 2010).

A membrane-based process scheme for the purification, fractionation, and concentration of phenolic compounds from wine wastewaters is depicted in Fig. 1. The purification step devoted to the removal of undesirable compounds (such as fats, proteins, and sugars) and microorganisms is based on the use of ultrafiltration (UF) membranes.

The use of appropriate nanofiltration (NF) membranes allows for obtaining fractions enriched in phenolic compounds. The final concentration step with removal of the extracting solvent (as permeate) is performed by reverse osmosis (RO).

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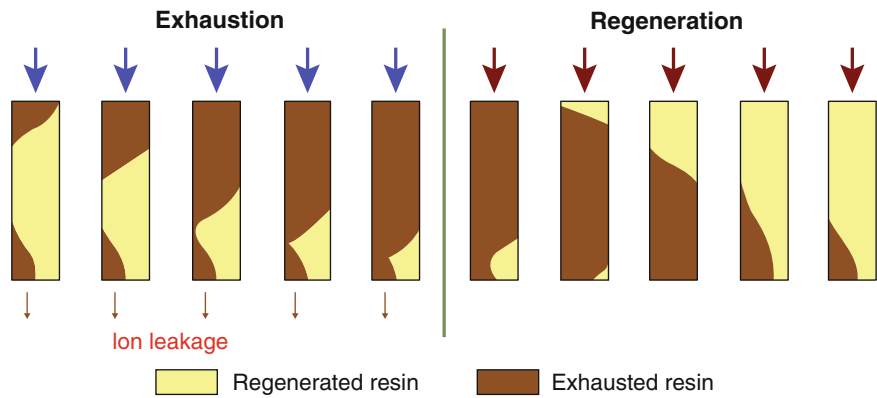
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Regeneration of the Ion-Exchange Resin

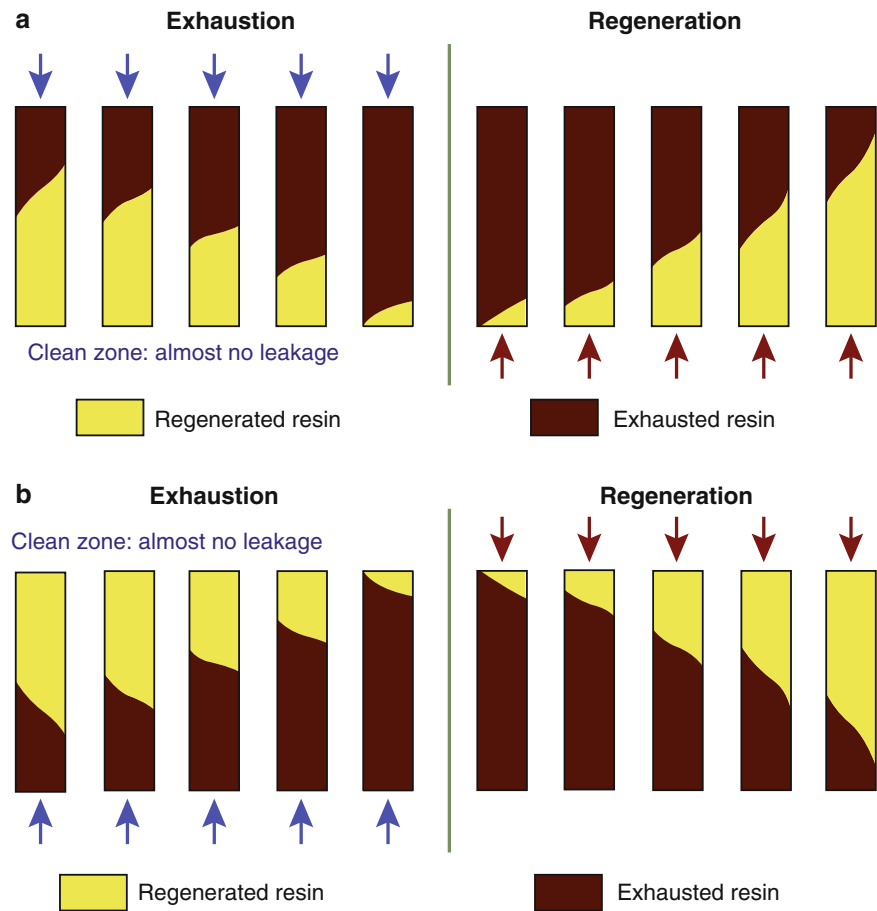
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Regeneration of the ion-exchange resin is the procedure for recovering the ion-exchange capabilities of exhausted ion-exchange resins. Most ion-exchange resins are used in columns. Ion-exchange operation is basically discontinuous: a loading phase, called service run, is followed by regeneration of the exhausted resins (Calmon 1986). Regeneration ratio is calculated as the total amount of regenerant (in equivalents) divided by the total ionic load (also in equivalents) during one cycle. It is also equal to the number of eq./L regenerant per eq./L of resin operating capacity. A (theoretical) regenerant ratio of 1.00 (i.e., 100 %) would correspond to the stoichiometric quantity. Nevertheless, all resins need a certain excess of regenerant above the stoichiometric



Regeneration of the Ion-Exchange Resin, Fig. 1 Illustration of co-flow regeneration (CFR) (Dardel and Arden 2008)



Regeneration of the Ion-Exchange Resin, Fig. 2 Illustration of reverse flow regeneration (RFR), including (a) upflow loading and downflow regeneration and (b) downflow loading and upflow regeneration (Dardel and Arden 2008)

quantity. The regeneration ratio is influenced by the technological process, the type and amount of regenerant, etc. There are two main methods for the regeneration process (Dardel and Arden 2008): (1) co-flow regeneration, where the fluids are flowing from the top to the bottom of the column both during the service run and during regeneration (Fig. 1), and (2) reverse flow regeneration, where the fluids are flowing alternatively upward and downward during service and regeneration (Fig. 2). Traditional regenerants are salts (such as NaCl, KCl, NH_4Cl), acids (HCl, H_2SO_4 , HNO_3 , acetic acid, citric acid), and alkali (NaOH, KOH, NH_3 , Na_2CO_3). For instance, NaCl is normally used to regenerate SAC resins in the softening process. SAC resins need to be regenerated with a strong acid for the purpose of decationization, and SBA resins are always regenerated with NaOH in the demineralization process. The disadvantages of the use of traditional regenerants are the low regeneration efficiency and the discharge of large amount of wastewater, leading to serious environmental pollution and resource waste. Improvement methods include (1) the recovery of the discharged wastewater; nanofiltration can be utilized for recovery of the wastewater, or the waste can be used to produce composite flocculant; (2) the modification of the regenerants; alcohol, ketone, and surfactant are added, or new regenerants are developed; and (3) the strengthening of the regeneration process. Ultrasonic, microwave, electrodiagnosis, or thermal treatment is applied for the strengthening.

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Regenerative Medicine

- [Bioartificial Organs, Membrane Operations of](#)
- [Tissue Engineering, Membrane Operations of](#)

Regenerative Medicine by Membrane Operations

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According to the definition given by Daar and Greenwood in 2007, *regenerative medicine* “is an interdisciplinary field of research and clinical applications focused on the repair, replacement or regeneration of cells, tissues or organs to restore impaired function resulting from any cause, including congenital defects, disease, trauma and ageing” (Daar and Greenwood 2007).

At the basis of regenerative medicine, there is an interdisciplinary approach that combines the contribution of different scientific branches such as stem cell biology, developmental biology, gene therapy, tissue engineering, and material sciences. This short definition will be mainly focused to the contribution given to regenerative medicine by tissue engineering and material sciences through the development and the introduction of membrane constructs and membrane operations. The development of new membrane systems allowed to elicit specific cell responses and to keep functional differentiated cells satisfying one of the most prominent issues in the field of regenerative medicine. The literature reports different approaches of membrane systems that use cell cultures in a therapeutic device or as in vitro model system for the screening of new therapeutic molecules on cell metabolism.

Within the membrane system, the cells proliferate, migrate, and differentiate into the specific

tissue while secreting the extracellular matrix (ECM) components required to create the tissue. It is evident, therefore, that the choice of the material is essential for the development and replication of an appropriate microenvironment for controlling and directing the cellular behavior and promoting specific cell interactions. It has been demonstrated that the suitability of polymeric membranes for regenerative medicine purposes is highly dependent on the tissue that needs to be engineered. The histological, physiological, and biomechanical properties of each tissue determine the success of the regenerative process, therefore restricting the choice of the material suitable for the specific application. When materials are implanted into the body, cells encounter a very unfamiliar environment that could negatively affect their viability. The use of polymeric membranes allows to overcome this issue, representing an ideal substrate for regenerative medicine application, since membranes can mimic the extracellular matrix with which cells interact allowing the organization of the cells into a three-dimensional architecture. The great advantage of using polymeric membranes in a regenerative medicine application is the possibility to tune the surface structures in order to provide the tissue-specific cues. Increasing cell affinity can be achieved by binding to the membrane surface-specific biomolecules that stimulate the specific cell substrate interaction able to drive cell behavior toward the tissue regeneration. An example of mimicking the natural ECM of surface modification is given by the incorporation of signal peptide such as RGD (Arg-Gly-Asp) which is a peptide with a characteristic sequence of many adhesive extracellular matrix proteins and can bound many integrin receptors. This kind of modification, thus, facilitates cell recognition and cell recruitment leading to tissue regeneration. An example of RGD-modified membrane is the bio-functionalization to improve blood biocompatibility and tissue regeneration promotion properties of vascular graft. Biodegradable RGD-modified (Zheng et al. 2012) PCL tubular grafts have been tested both *in vitro* and *in vivo* in terms of

adhesion of platelet adhesion, infiltration, endothelialization, and as final step smooth muscle regeneration. After *in vivo* implantation in the carotid arteries of rabbits for 2 and 4 weeks, on the RGD-modified graft was observed a consistent reduction of platelet adhesion without any aggregation indicating an improvement of the graft biocompatibility. The presence of the biomolecule on the membrane surface promoted a deep cell colonization within the tubular scaffold, and the PCL-RGD graft was completely covered by a layer of endothelial cells, and a smooth muscle regeneration was observed, with characteristics similar to the one of the native artery.

Polymeric membranes, for their selective transport properties, can be also used for cell encapsulation, representing a possible tool for cell transplantation and release of specific molecules (growth factors, proteins, etc.) opening new application in regenerative medicine. The polymeric membrane immunoisolates the entrapped cells preventing the direct contact with the host immune system component; moreover, governing the mass transport of molecules, it recreates a suitable micro-environment allowing the perfusion of nutrients toward the cell compartments and the controlled delivery of the specific products. The cells encapsulated within the polymeric membranes can have different sources of origin according to the specific application and therefore can have a broad use, treating different pathological conditions in order to promote the regeneration of the organ functions such as in the central nervous system disease, diabetes, or liver failure and induce cartilage and bone regeneration as well as cardiovascular tissue regeneration (Hernández et al. 2010).

One innovative approach is the cell encapsulation using microfibers that can contain a variety of cells (Kang et al. 2014). An innovative approach (Onoe et al. 2013) led to the realization of functional microfibers able to form cell fibers that have been characterized for muscle, blood vessels, or neuronal network formation.

Within the wide field of regenerative medicine, in which membranes represent a support and a template able to promote the specific tissue district

regeneration, a peculiar example is given by the use of membranes as neuronal scaffold, either for the development of peripheral nerve conduits or to be used as a guidance in spinal cord injuries (SCI). In order to bridge a peripheral nerve gap, the three-dimensional structure of the membrane scaffold plays a significant role in neuron adhesion and neurite outgrowth; as a result nerve guidance channels (NGCs), such as hollow fiber membranes, have been deeply investigated for the promotion of nerve regeneration. Along single tube membranes, also multichannel tubular membranes have been proposed with the aim to mimic the more complex distribution of the bundle of nerve fibers.

In a nerve tube design, the membrane can be made up of biodegradable and nondegradable polymer, and good mechanical properties are one of the major issues in order to offer an adequate support to the cells in contact with. Good permeability qualities are necessary in order to allow the diffusion of nutrient and oxygen since the pore size and distribution determine the mass transfer of bioactive molecule that influences the nerve regeneration process. Another important aspect in the design of a membrane nerve guidance is represented by the topographical cues such as the recreation of highly aligned membrane scaffold that are able to promote the longitudinal elongation of the nerve toward the distal nerve stump in order to fill the gap. For instance, the use of aligned nanofibrous nerve conduits can enhance axon regeneration in rat sciatic nerve transection model.

Further strategies that are aimed to enhance the membrane performance in promoting the nerve regenerative process are represented by the incorporation of biochemical cues such as neurotrophic factors (NFs) and extracellular matrix (ECM) proteins which are delivered at the local lesion site in order to sustain tissue regeneration (Marquardt and Sakiyama-Elbert 2013; Gu et al. 2014).

Neuronal tissue regeneration is just one of the many applications of membrane systems for regenerative medicine. Current strategies for the development of an ideal membrane support for tissue regeneration are based on the combination of physiochemical and biological parameters that

are needed to mimic the *in vivo* microenvironment, which generates a functional product matching the clinical standards.

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Rejection

- [Characterization of Porous and Dense Membranes](#)
- [Permselectivity](#)

Release of Antimicrobial Agent

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Antimicrobial packaging is produced by adding active ingredients in the packaging system or

coating/immobilizing active agent onto the surface and/or using actively functional polymers that satisfy conventional packaging requirements. The use of antimicrobial packaging has received great attention since these types of systems provide high food quality, safety, and long shelf-life by reducing, inhibiting, or retarding the growth of microorganisms. Traditionally, antimicrobial agents are directly mixed into the initial food formulations in an excess amount since this approach may result in a decrease in the concentration of the antimicrobial agent on the food surface due to its diffusion into the interior parts of the food. Antimicrobial packaging offers an alternative way to overcome these limitations.

Controlled release of the antimicrobial agent from the film to the food surface is one of the most important desired properties of the antimicrobial packaging materials. A rapid release causes fast consumption of the agent in a short period of time; thus, protection of the food ceases, on the other hand, spoilage reactions on the food surface may start if the release rate of the antimicrobial agent from the film is too slow. Controlled release of the antimicrobial agent can overcome this limitation by continuously replenishing it to the food surface, compensating for the consumption or degradation of active compounds. Controlled release of drugs has been used for some time, and procedures for achieving desirable rates are well established, on the other hand, research on the development of food packaging films with controlled release properties are limited. Strategies used to control the release rate of antimicrobial agent from the packaging are mainly based on changing the degree of cross-linking (Buonocore et al. 2004) or asymmetric structure of the film (Gemili et al. 2009) or forming multilayer structured films (Han and Floros 1998). The release of the antimicrobial agent from the film involves first diffusion within the film toward the film/food interface, mass transfer across the interface, and dispersion into the bulk food. In most cases, diffusion in the film is the slowest and the rate-controlling step. In laminated multilayer systems, the outer layer is generally used to prevent loss of

the antimicrobial agent to the environment. The matrix layer contains antimicrobial agent and has usually amorphous structure to provide space for entrapping large amount of the antimicrobial agent and fast diffusion of the antimicrobials. The inner layer is the key layer to control the initial lag period and the flux of the antimicrobial agent. Therefore, the thickness of this layer and its structural characteristics are optimized to control the release rate of the antimicrobial agent. When highly swellable polymers are used as packaging material, in addition to diffusion of the antimicrobial agent, diffusion of water into the matrix and the rate of swelling of the matrix are also important factors that control the release rate of the antimicrobial agent. In cases where the characteristic diffusion time is lower than the relaxation time of the polymer, relaxation becomes the limiting phenomena controlling the solvent uptake, consequently the release of the antimicrobial agent. Food packaging materials based on proteins or polysaccharides are usually charged at the pH of the release medium. When both the antimicrobial agent and the food packaging material are charged, then the release rate depends on the pH of the release medium. In this case, the release of the agent occurs only if both the agent and the polymer are similarly charged since this condition promotes repulsion between them. Thus, the choice of the polymer matrix for the charged antimicrobial agent should be done based on the pH of the target food.

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Reliability in Gas Separation

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The reliability takes into account the on-stream factors which can cause unscheduled shutdowns. It is an important project consideration, particularly if the process is a primary source of make-up hydrogen to a hydroprocessor or other main-stream refinery processes (Miller and Stöcker 1989; Brunetti et al. 2010).

Membrane systems are extremely reliable with respect to the on-stream factor. The membrane separation process is continuous and has few control components which can cause a shutdown. Typically, the response to unscheduled shutdowns is rapid. Absorption systems are moderately reliable. The large equipment associated with the process for avoiding the formation of degradation and corrosion products and the presence of particles can cause unexpected shutdowns.

PSA systems are also moderately reliable. The numerous valves associated with the process can induce unscheduled shutdowns. The new PSA are designed with alternate modes of operation, in which 100 % of design capacity can be achieved while bypassing any failed valve or instrument, with only a slight loss of recovery. Failures are automatically detected and bypassed by the microprocessor-based control system. However, stronger and periodic control cycles are required.

The cryogenic process is considered by refiners to be less reliable than the PSA or membrane processes; this is mainly due not to the process itself but to the need for feed pretreatments. Failure of the pretreatment system usually results in contaminants freezing in the cold box, leading to shutdown. In this case, a “thaw” is necessary prior to restart. The pretreatment system itself is often more complex than the cryogenic system.

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Removal of Antibiotics from Wastewaters by Membrane Operations

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Antibiotics are persistent pollutants present in wastewaters originating from the pharmaceutical industry, but, due to their extensive human and veterinary use, they have also been found in municipal wastewaters. It has been observed that conventional activated sludge (CAS) wastewater treatment is not sufficient for the removal of antibiotics, and their presence in wastewater effluents is considered one of the causes of the emergence of antibiotic-resistant organisms. Several approaches have been proposed for the removal of antibiotics from wastewaters, the more promising being membrane bioreactors (MBRs), membrane filtration, and advanced oxidation processes or a combination of the above (Michael et al. 2013).

Conventional wastewater plants were not designed to treat pharmaceutical compounds and, in particular, antibiotics, due to their highly variable chemical structure and properties. As a consequence, the efficiency of antibiotic removal varies according to the different antibiotic molecule. Another important issue is antibiotic concentration in the effluents, which depends on the origin of the wastewater stream. In wastewaters

coming from the pharmaceutical industry, the antibiotic concentration may be sufficiently high to require a pretreatment before the biological wastewater treatment. This could be necessary, because the presence of antibiotics restrains microorganism growth and may hamper the biological treatment processes (Lefebvre et al. 2014).

Among the suitable pretreatments, an important role is played by membrane processes with nanofiltration and reverse osmosis being more effective than ultrafiltration in antibiotic rejection. Removal rates for NF depend on the target antibiotic molecule, with removal higher than 80 % and as high as 95 % for macrolides. RO has shown 100 % removal rates, but higher energy requirements for the process and several drawbacks which include membrane compaction, fouling, and biological growth. It has been shown that the performance of RO in wastewater filtration can be dramatically improved by including a UF/NF prefiltration step (Zhang et al. 2006).

In municipal wastewaters, antibiotics and their metabolites are excreted by humans after administration and they are present in different varieties, but with lower concentration. In this case, application of either MBR systems, or advanced processing downstream of the conventional biological treatment, is crucial for antibiotic removal before effluent discharge. MBRs are more effective in the removal of antibiotics than CAS systems even if their cost is higher. The concentrate stream of the MBR system contains all the removed antibiotics, which can be efficiently degraded by ozonation (Senta et al. 2011; Liu et al. 2014).

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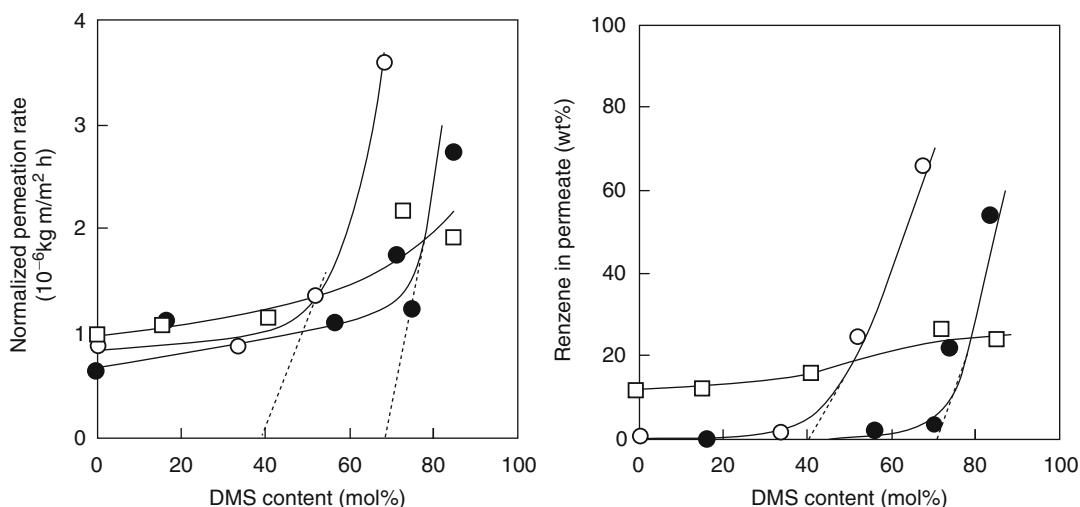
Removal of Dissolved VOCs from Aqueous Solutions (Pervaporation Application)

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Organic liquid/water selective membranes are effective for the removal of organics in water and recovery of organic solvents from water. These membranes can contribute to the environmental problem and effective use of organic solvents.

The removal of volatile organic compounds (VOCs) such as benzene and chloroform from aqueous benzene and chloroform solutions using poly(methyl methacrylate)-poly(dimethylsiloxane) (PMMA-g-PDMS), poly(ethyl methacrylate)-PDMS (PEMA-g-PDMS), and poly(n-butyl methacrylate)-PDMS (PBMA-g-PDMS) graft copolymer membranes was investigated by pervaporation (PV). When aqueous solutions of dilute VOCs were permeated through the PMMA-g-PDMS and PEMA-g-PDMS membranes, these membranes were Bz/H₂O- and CHCl₃/H₂O selective. The permeation and separation characteristics of the PMMA-g-PDMS and PEMA-g-PDMS membranes changed drastically at a DMS content of about 40 mol% and 70 mol%, respectively, as shown in Fig. 1. The permeation rate and VOC/water selectivity of the



Removal of Dissolved VOCs from Aqueous Solutions (Pervaporation Application), Fig. 1 Effects of the DMS content on the benzene concentration in the permeate and normalized permeate for an aqueous solution of

0.05 wt.% benzene through PMMA-g-PDMS (○), PEMA-g-PDMS (●), and PBMA-g-PDMS (□) membranes during PV

PBMA-g-PDMS membranes, however, increased gradually with increasing DMS content, unlike those of PMMA-g-PDMS and PEMA-g-PDMS membranes. Furthermore, TEM observations revealed that the PMMA-g-PDMS and PEMA-g-PDMS membranes had microphase-separated structures, consisting of a PDMS phase and a poly(alkyl methacrylate) phase. On the other hand, the PBMA-g-PDMS membrane was homogeneous. It was found that the permeability and selectivity of these graft copolymer membranes for treatment of aqueous VOC solutions by PV were significantly related to a PDMS continuous layer in the phase-separated structure (Uragami et al. 1999, 2001a).

Hydrophobically surface-modified membranes were prepared by adding a fluorine-containing graft copolymer to a microphase-separated membrane consisting of PDMS and PMMA to improve organic component selectivity. Contact angle measurements and X-ray photoelectron spectroscopy (XPS) revealed that the addition of a fluorine-containing copolymer produced a hydrophobic surface at the air side of the membrane due to surface localization of the fluorinated copolymer. It was apparent from TEM that adding a fluorine-containing copolymer of less than small

amount did not affect the morphology of the microphase-separated membrane. However, adding a fluorine-containing copolymer over a certain amount resulted in a morphological change, from a continuous PDMS phase to a discontinuous PDMS phase. The addition of a small amount of fluorine-containing copolymer to the microphase-separated membranes enhanced both their permeability and Bz/Chx selectivity for a dilute aqueous solution of benzene during PV because of their hydrophobic surfaces and microphase-separated structures. Specifically, the microphase-separated membrane with a small amount of fluorine-containing copolymer concentrated an aqueous solution from 0.05 to 70 wt.% benzene and, therefore, removed the benzene from water very effectively (Miyata et al. 2001).

PMMA-g-PDMS and PMMA-*b*-PDMS membranes containing tert-butylcalix[4]arene (CA) (CA/PMMA-g-PDMS and CA/PMMA-*b*-PDMS) were applied to the removal of benzene from a dilute aqueous solution of benzene by PV (Uragami et al. 2006). When an aqueous solution of 0.05 wt.% benzene was permeated through CA/PMMA-g-PDMS and CA/PMMA-*b*-PDMS membranes, these membranes showed high

Bz/Chx selectivity. Both the permeability and Bz/H₂O selectivity of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes were enhanced by increasing the CA content, due to the affinity of CA for benzene. The permeability and Bz/H₂O selectivity of CA/PMMA-*b*-PDMS membranes were much greater than those of CA/PMMA-*g*-PDMS membranes. TEM observations revealed that both the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes had microphase-separated structures consisting of a PMMA phase and a PDMS phase-containing CA. The microphase-separated structure of the latter membranes was much clearer than that of the former and was lamellar. The distribution of CA in the microphase-separated structure of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes was analyzed by differential scanning calorimetry (DSC), and CA was distributed in a PDMS continuous layer in microphase-separated structure (Uragami et al. 2001b, 2006).

It was found that a continuous PDMS layer in PMMA-*g*-PDMS and PMMA-*b*-PDMS membranes plays an important role for the removal of VOCs from water. For the purpose of constructing the membrane matrix from PDMS component mainly, polydimethylsiloxane dimethylmethacrylate macromonomer (PDMSDMA) was selected as a membrane material. The effects of cross-linkers of the cross-linked PDMS membranes derived from PDMSDMA and divinyl compounds were investigated, on the PV characteristics of the removal of benzene from an aqueous solution of dilute benzene. When an aqueous solution of 0.05 wt.% benzene was permeated through the cross-linked PDMSDMA membranes, they showed high Bz/H₂O selectivity. Both the permeability and Bz/H₂O selectivity of the membranes were enhanced with increasing divinyl compound content as the cross-linker and were significantly influenced by the kind of divinyl compound. PDMSDMA membranes cross-linked with divinyl siloxane (DVS) showed very high membrane performance during PV. The best normalized permeation rate, separation factor for Bz/H₂O selectivity, and PV separation index (PSI) (Huang and Rhim 1991) which is the product of the permeation rate and the separation factor

and can be used as a measure of the membrane performance during PV, of a PDMSDMA-DVS membrane, were 1.96×10^{-5} mkg (m²h)⁻¹, 98, and 192, respectively (Uragami et al. 2003). When divinyl perfluoro-*n*-hexane (DVF), which is much more hydrophobic, was employed as a cross-linker of PDMSDMA, the best normalized permeation rate, separation factor for Bz/H₂O selectivity, and PSI of a PDMSDMA-DVF membrane were 1.72×10^{-5} mkg(m²h)⁻¹, 4,316, and 7,423, respectively (Ohshima et al. 2005a).

In Table 1, the permeation and separation characteristics of various polymer membranes consisting of the PDMS components are compared under the same PV condition: feed solution, an aqueous solution of 0.05 wt.% benzene; permeation temperature, 40°C; and pressure of permeation side, 1.33 Pa. As can be seen in Table 1, both the normalized permeation rate and the Bz/H₂O selectivity of each of the CA/PDMSDMA-DVB, CA/PDMSDMA-DVS, and CA/PDMSDMA-DVF membranes were improved as compared to each of the PDMSDMA-DVB, PDMSDMA-DVS, and PDMSDMA-DVF membranes. Although the separation factors of the CA/PDMSDMA-DVB and CA/PDMSDMA-DVS membranes were lower than that of the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes, the PSI of the former membranes was much greater than that of the latter one. In Table 1, it was found that the addition of CA into the cross-linked PDMSDMA membranes cross-linked with a suitable cross-linker is significantly effective to obtain higher permeation and separation characteristics. A CA/PDMSDMA-DVF membrane with DVF of 90 mol% and CA of 0.4 wt.% showed the best membrane performance, i.e., the normalized permeation rate, separation factor for Bz/H₂O selectivity, and PSI were 1.86×10^{-5} mkg(m²h)⁻¹, 5,027, and 9,350, respectively.

The air stripping removal of VOCs such as toluene and phenol from water by microporous polypropylene (PP) hollow fibers was studied. The VOC stream passed through the lumen side of the module, while air (stripping gas) flowed across the shell side. Experiments were performed

Removal of Dissolved VOCs from Aqueous Solutions (Pervaporation Application), Table 1 Performance for Bz/H₂O of various membranes containing PDMS component

Various PDMS membranes ^a	$\alpha_{\text{sep.}}$	$\alpha_{\text{sorp.}}$	$\alpha_{\text{diff.}}$	NPR ^b	PSI ^c	Refs
	Bz/H ₂ O	Bz/H ₂ O	Bz/H ₂ O			
PMMA	53	422	0.13	0.29	16	Uragami et al. (2001a)
PMMA-g-PDMS ^d	620	739	0.86	0.13	226	Uragami et al. (2006)
CA/PMMA-g-PDMS ^e	1,772	1,267	1.40	0.71	1,240	Uragami et al. (2006)
PFA-g-PDMS/PMMA-g-PDMS ^f	4,492			0.64	2,879	Miyata et al. (2001)
PDMSDMMMA-DVB ^g	3,171	1,436	2.21	1.46	4,629	Uragami and Ohshima (2003)
PDMSDMMMA-DVS ^h	2,886	1,270	2.46	1.96	5,656	Uragami and Ohshima (2003)
PDMSDMMMA-DVF ⁱ	4,316	1,804	2.49	1.72	7,423	Ohshima et al. (2005)
CA/PDMSDMMMA-DVB ^j	4,021	1,689	2.18	1.75	7,037	Ohshima et al. (2005)
CA/PDMSDMMMA-DVS ^k	3,866	1,620	2.39	1.97	7,616	Ohshima et al. (2005)
CA/PDMSDMMMA-DVF ^l	5,027	1,998	2.52	1.86	9,350	Ohshima et al. (2005)

^aPV experimental conditions: feed solution, an aqueous solution of 0.05 wt.% benzene; permeation temperature, 40 °C; pressure of permeation side, 1.33 Pa

^bNormalized permeation rate [10^{-5} mkg(m²h)⁻¹]

^cPV separation index (NPR $\times$ $\alpha_{\text{sep. Bz/H}_2\text{O}}$)

^dPDMS content 74 mol%

^ePDMS content 74 mol%; CA content 40 mol%

^fPDMS content 74 mol%; PFA-g-PDMS content 1.2 wt.%

^gDVB content 80 mol%

^hDVS content 90 mol%

ⁱDVF content 90 mol%

^jDVB content 80 mol%; CA content 0.5 wt.%

^kDVS content 90 mol%; CA content 0.5 wt.%

^lDVF content; CA content

at different liquid flow rates (8–16 cm³ min⁻¹), gas flow rates (60–180 cm³ min⁻¹), feed VOC concentrations (100–1,000 ppm), and temperatures (24–35 °C). The removal was more effective when feed VOC level and liquid or gas flow rate increased. The applicability of a mass transfer model that considers diffusion in the liquid layer, membrane, and gas layer under steady state was checked. Unlike phenol with a very small dimensionless Henry's law constant (equilibrium gas concentration divided by liquid concentration) and a relatively low amount of sorption on PP fibers, the measured overall mass transfer coefficients for toluene reasonably agreed with those predicted from the model. The large deviation observed for phenol indicated unsteady state nature, likely due to its small concentration difference between air and liquid phase/fiber matrix (Juang et al. 2005).

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Response Surface Methodology (RSM)

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RSM consists of a collection of mathematical and statistical analyses used in the development of an adequate functional relationship between a response of interest y (referred to as response variables) and a number of associated factors (or input) denoted by $x_1, x_2, \dots, x_k$. For example, this approach can be exploited to find the levels of temperature (x_1), pressure (x_2), and flow rate (x_3) that maximize the permeate flux (y) in a membrane process. Therefore, permeate flux is a

function of the levels of temperature, pressure, and flow rate as follows:

$$y = f(x_1, x_2, x_3) + \varepsilon \quad (1)$$

where ε represents the random experimental error or noise observed in the response y . If the expected response is denoted by $E(y) = f(x_1, x_2, x_3) = \eta$, then the surface represented by

$$\eta = f(x_1, x_2, x_3) \quad (2)$$

is called as response surface.

Usually, a second-order model (Eq. 3) is used to find a suitable approximation for the true functional relationship between y and the set of selected factors:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j} \sum_j \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where y is the response variable (permeate flux for the previous example), β is the model constant, and ε is the residual (error or noise). The second-order model includes the linear x_i , quadratic x_i^2 , and interaction $x_i x_j$ effect for each factor (Montgomery 2001).

The main scope of RSM approach is to determine which factors and interactions are significant in contributing to the response being measured and those factors and interactions that are insignificant and do not contribute to either a particular response. In addition, an important objective is to determine the optimum settings of $x_1, x_2, \dots, x_k$ that result in the maximum, minimum, or target response over a certain region of interest.

In order to achieve these objectives, a series of n experiments should be carried out previously. In these experiments, the response y is measured for specified settings of the factors. The totality of these settings constitutes the so-called response surface design, which can be represented by a matrix, denoted by D , of order $n \times k$ called the design matrix:

$$D = \begin{bmatrix} x_{11} & x_{12} & \dots & x_{1k} \\ x_{21} & x_{22} & \dots & x_{2k} \\ \vdots & \vdots & \dots & \vdots \\ x_{n1} & x_{n2} & \dots & x_{nk} \end{bmatrix}$$

where x_{ui} denotes the u th design setting of x_i ($i = 1, 2, \dots, k$; $u = 1, 2, \dots, n$). Each row of D represents a point, referred to as a design point, in a k -dimensional Euclidean space (Khuri and Mukhopadhyay 2010).

It is crucial the proper choice of design in any response surface investigation, considering concepts such as orthogonality and rotatability, which affect the quality of model prediction. The most common designs applied in RSM are central composite design (CCD) and Box-Behnken design. CCD is obtained by augmenting a first-order design, namely, the 2^k factorial, with additional experimental runs, namely, the 2^k axial points ($-\alpha$ and α) and center-point (0) replications. The first-order design serves in a preliminary phase to get initial information about the response system and to assess the importance of the factors in a given experiment. The additional experimental runs are chosen for the purpose of getting more information that can lead to the determination of optimum conditions on the control variables using the second-degree model. On the other hand, Box-Behnken design provides three levels for each factor and consists of a particular subset of the factorial combinations from the 3^k factorial design. This design is popular in industrial research because it is an economical design and requires only three levels for each factor: minimum (-1), middle (0), and maximum (1); therefore, few experiments are needed. Other second-order designs are available but they are not frequently used as the ones already mentioned. Some of these designs include Hoke designs, Box-Draper saturated designs, uniform shell designs by Doehlert, and hybrid designs by Roquemore (Khuri and Mukhopadhyay 2010).

Once completed all the experiments and collected all the data for each response variables, it is possible to determine, by using the analysis of variance (ANOVA), the significance of each factor as well as interaction and quadratic effect. The

second-order model should be evaluated considering correlation coefficient (R^2), normal distribution of the residual, autocorrelation, and lack-of-fit test. If the model is adequate to describe the observed data, at the selected confidence level, the results can be represented by using contour plots, Pareto chart, main effect plot, interaction plot, and residual plot as well.

The determination of optimal conditions for one or multiple responses is determined by using the desirability function (DF). This method finds operating conditions that provide the most desirable responses. It is based on the conduction of experiments and fitting response models (y_k) for all k responses, the definition of individual desirability functions for each response (d_k), and the maximization of the overall desirability in comparison with controllable factors. For each response $y_k(x_i)$, a desirability function $d_k(y_k)$ assigns numbers between 0 and 1 to the possible values of y_k , with $d_k(y_k) = 0$ representing a completely undesirable value of y_k and $d_k(y_k) = 1$ representing a completely desirable or ideal response value. Depending on whether a particular response y_i has to be maximized, minimized, or assigned to a target value, different desirability functions $d_k(y_k)$ can be used. The individual desirability functions from the considered responses are then combined to obtain a total desirability function, $D(0 \leq D \leq 1)$ (Ruby-Figueroa et al. 2011).

This approach has resulted to be useful for developing, improving, and optimizing processes in which one or multiple responses of interest are influenced by several variables (factors) and the objective is to optimize these responses.

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Responsive Membranes

► Magnetically Responsive Membranes

Retentate

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The retentate is the whole mass leaving the membrane on the same side as the feed. It is collected in a volume or as a stream, leaving the membrane module in a batch or continuous operations, respectively. Together with the permeate, the retentate is one of the two outlets of a membrane unit. The other two streams are the feed and, optionally, the sweep.

Since no species can quantitatively/totally pass through the membrane except in the case of infinite permeation driving force, generally, it contains all the species feed to the membrane module.

Reuse of Paper Mill Effluents, Membranes for

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The reduction of fresh water consumption in industry, particularly in the pulp and paper sector, is one of the main sustainable issues nowadays, and although water reuse within the process will reduce water consumption, the total closure of water circuits is limited by the increase of contamination load in process water, and moreover,

fresh water intake is always needed to compensate water losses. Therefore, the improvement of fresh water savings is moving to the regeneration and reuse of the final effluent of the mill, to obtain high quality water for replacing fresh water at critical points, and to the use of alternative fresh water sources as reclaimed water from municipal wastewater treatment plants (Ordóñez et al. 2014, 2010).

For treating the final effluent, paper mills operate different systems depending on the type and load of the wastewater. Usually, an equalization is performed followed by solids removal by physical or physicochemical methods. Subsequently, a biological treatment for the removal of dissolved biodegradable organic compounds is performed. Although the more applied biological treatment is aerobic, mainly activated sludge, nowadays anaerobic digestion is taking advantage due to its viability for producing energy and the reduction of sludge production (de Lemos Chernicharo 2007).

In this framework, to avoid any health and operational risk, membrane processes are being implemented as final tertiary treatment. In this sense, to control biofouling in the subsequent membrane treatments anaerobic treatment must be combined with aerobic treatment to reduce soluble organic matter in a higher extent that is 95 % (Bajpai 2000; de Lemos Chernicharo 2007). Moreover, effluents from biological treatments of paper mills are characterized by high solids concentrations, including fibers and bacteria flocs, among other residues of production. Hence, microfiltration (MF) or ultrafiltration (UF) are the necessary pretreatment for the wastewater inflowing a final nanofiltration (NF) or reverse osmosis (RO) unit (Speth and Reiss 2005). While MF is suitable for removing suspended solids, including larger microorganisms like protozoa and bacteria, UF may even remove viruses and organic macromolecules down to approx. 0.02 μm (Mallevialle et al. 1999; Speth and Reiss 2005). In general, UF is highly used in treatment plants reclaiming wastewater worldwide, and membrane bioreactors (MBRs) are taking advantage in different urban and industrial

applications because they operate in a submerged design, which requires low trans-membrane pressures (TMP), thus minimizing the effects of fouling and the problems related to filamentous bulking, so usual in paper mills (Judd 2006; Judd and Jefferson 2005; Ordóñez et al. 2014). Moreover, they may incorporate a higher dried solid concentration ($8\text{--}15\text{ g} \cdot \text{L}^{-1}$) than conventional activated sludge ($3\text{--}5\text{ g} \cdot \text{L}^{-1}$). Therefore, they produce less biological sludge. These properties also lead to lower hydraulic retention times and/or volumes required to perform the biological treatment in comparison to conventional systems (Judd 2006). Although, it is needed to consider that encased dead-end mode UF systems may entail a lower operational cost (Ordoñez et al. 2010, 2011).

As final step, to ensure a final water free of pathogens and of guaranteed quality for permitting stable operation conditions (mainly conductivity reduction), RO systems are recommended in any treatment train. However, in these systems scaling and fouling phenomena may cause decline in water production rates, low permeate quality, unsteady-state operation conditions, and serious damages in the membranes (Asano et al. 2007; Bickerton et al. 2011; Bonnelye et al. 2008; Judd and Jefferson 2005; Mallevialle et al. 1999). These are the current bottlenecks that paper mill managers must carefully deal, mainly with the scaling associated to silica and calcium compounds.

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Reverse Electrodialysis (RED)

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Synonyms

Electrodialysis reversal

Electrodialysis reversal (EDR) is a modification of the simple ED commercially introduced by Ionics in 1967 to overcome major electrodialysis shortcomings such as membrane fouling and scaling. In the EDR system, the polarity of the direct current applied to the ED stack electrodes is reversed at specific time intervals ranging from a few minutes to several hours (typically two to four times per hour) (Meller 1984). If the polarity is reversed, the negatively charged colloids will now be removed from the anion-exchange membrane back into the bulk and the membrane properties are restored. Not only colloidal materials but also freshly precipitated sparingly soluble salts are effectively removed from the membrane with this procedure before they can solidify.

In the reverse polarity operating mode, the hydraulic flow streams are reversed simultaneously with the reversed polarity, i.e., the diluate cell will become the concentrate cell and vice versa. During the reversal of polarity and flow streams, there is a brief period when the concentration of the desalted water exceeds the required product salinity. Therefore, the ED diluate outlet has a concentration sensor which controls an additional three-way valve. This valve diverts diluate with a too high concentration, the so-called off-spec product, into the ED concentrate or feed. Then, when the concentration drops to the specified value, the product flow is directed back to the product outlet. Thus, the necessity to clean the ED channels between changing the polarity causes some loss of overall efficiency as a certain amount of product is lost to the waste stream or has to be treated again. Employing the use of four-way valves instead of three-way ones enables one to decrease the amount of off-spec product during the reversal to some extent (Strathmann 2010).

In the classical EDR, the diluate and concentrate chamber dimensions as well as flow, and velocity of dilute and concentrate are equal. Thus, the concentrate is recycled to gain a high diluate recovery ratio. The resulting residence

time is thus very high, which limits the maximum permissible level of CaSO_4 and/or CaCO_3 supersaturation. The mean ion residence time (MIRTc) in a typical EDR design was estimated at ≥ 130 min (Myint et al. 2011). The resulting Langelier Saturation Index (LSI, determining the CaCO_3 precipitation risk) and CaSO_4 relative saturation level that are commonly used indices to control the scaling process are limited to 2.16 % and 200 %, respectively. The addition of mineral acid into the concentrate stream decreases the risk of CaCO_3 precipitation, while the addition of antiscalant, usually SHMP, shifts the scaling-free EDR operation to the region of gypsum saturation up to 300 % (Meller 1984). However, if comprehensive utilization of wastewater and controlled crystallization of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the concentrate stream is considered, then any chemical addition is not allowed. Thus, a further increase in saturation level may be achieved only by decreasing the concentrate residence time value (Turek et al. 2007).

In terms of unit costs of desalination, EDR is comparable to RO for waters with TDS < 3000 mg/L, but it is especially suitable for the treatment of waters and wastewaters with high scaling and fouling potential.

Cross-References

- [Electrodialysis](#)
- [Membranes for Blue Energy](#)
- [Reverse Electrodialysis in High Supersaturation Mode](#)

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Reverse Electrodialysis in High Supersaturation Mode

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Synonyms

Electrodialysis reversal in high supersaturation mode

The supersaturation level with sparingly soluble salts, mainly calcium carbonate and calcium sulfate, and resulting product water recovery in the classical electrodialysis reversal with recycling of ED concentrate are limited by a relatively long mean residence time in the concentrate loop (Myint et al. 2011). A substantial increase in scale-free operation at a high supersaturation level may be gained in a single-pass mode of operation only. In this case, the mean residence time (favorably accompanied by low variance of residence time distribution (RTD)) should be small when compared to nucleation time of crystallization of the sparingly soluble salt in question (Turek et al. 2006).

Electrodialysis was carried out in a single-pass mode with symmetric reversed polarity every 6–10 h. The problem of CaSO₄ precipitation was prevented by continuous removal of gypsum from

the brine in a separate precipitator, in which gypsum seeds were used to increase the rate of gypsum nucleation and significantly reduce the level of CaSO₄ supersaturation in the EDR concentrate (Korngold et al. 2005). It was found that antiscalant diminished the seeding effect on gypsum crystallization and increased the onset of crystallization time. Thus, it was demonstrated that the ED process combined with continuous CaSO₄ precipitation (in a separate precipitator) may be successfully carried out under a reverse polarity operation regime.

In a novel EDR design (Turek et al. 2006), different diluate and concentrate linear velocity values are applied instead of recirculation of concentrate. Thus, the concentrate's linear flow velocity is several times lower than the diluate's, so a certain diluate concentration decrement results in a several times higher increment in the concentrate salt concentration. At the same time, low residence time is gained due to a single-pass mode. The ED process with different diluate and concentrate flow velocities may be carried only when applying a thin, e.g., 0.19 mm, net spacer with high strand density that protects the membrane against bulging. The intermembrane distance also influences the rate of both diluate and concentrate salt content changes along the ED membrane. The amount of salt passing a certain membrane surface in a certain period of time results from the current density value. When added to a small volume of the solution, being inversely proportional to the intermembrane distance, it would increase its concentration to a large extent. The avoidance of concentrate recirculation and low mean residence time are the essential advantages of single-pass EDR. It was demonstrated that EDR in this mode can operate with no chemical addition at CaSO₄ saturation levels of Ca 500 % and +2.3 LSI (Turek et al. 2009, 2012). EDR carried out at small intermembrane distance and low residence time enables one to increase working time without changing the polarity and to decrease the ED

channel cleaning period between changing it. Both of these features result in an increase in product recovery and a reduction of the unit costs of desalination.

It was demonstrated that EDR in a single-pass mode can operate at a high supersaturation level which up till now has only been achieved with a chemical addition to the concentrate stream. The lack of antiscalants allows for the controlled crystallization of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 in the concentrate stream. In the case of waters containing calcium sulfate and calcium bicarbonate as dominant solutes (over NaCl), crystallization of the aforementioned species might decrease the total concentrate salinity to a large extent. This will allow zero-discharge technology to develop (Turek et al. 2007, 2009).

Cross-References

- [Electrodialysis](#)
- [Reverse Electrodialysis \(RED\)](#)

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Reversible Flux Decline

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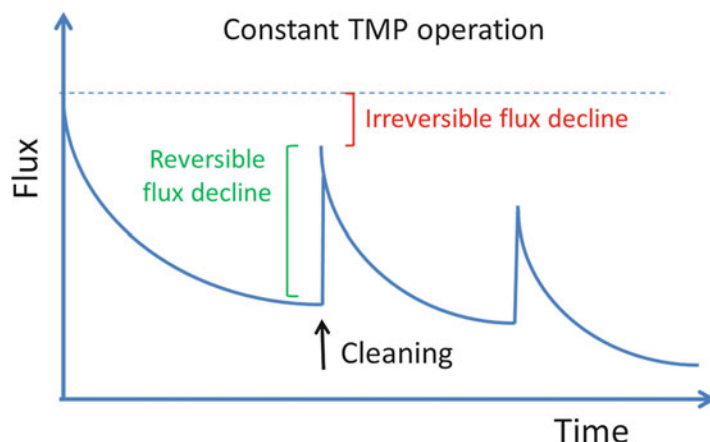
Synonyms

[Reversible fouling for constant pressure operation](#)

When constant transmembrane pressure (TMP) is applied to pressure-driven membrane processes, fouling formation on the surface results in flux decline. When operating conditions exceed a critical value, and/or when filtration is no longer sustainable, physical or chemical cleaning protocols are implemented to recover some of the original hydraulic performances. Specifications from membrane suppliers (or original equipment manufacturer (OEM) data) provide an approximation for the level of flux to be obtained for a given driving force.

The level of flux reversibility is proportional to the strength of the cleaning process and is generally slightly lower than 100 %. In other words, cleaning strategy can generally not guarantee full recovery of flux performances. The fraction of the flux recovered during cleaning is defined as the reversible flux decline (Fig. 1).

Reversible Flux Decline,
Fig. 1 Typical cycles of
 flux decline during filtration
 and partial reversibility
 during cleaning



Cross-References

- [Physically Reversible Fouling](#)
- [Reversible Fouling](#)
- [Reversible Fouling Resistance](#)

Reversible Fouling

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Synonyms

Reversible flux decline

Fouling remains one of the main drawbacks of pressure-driven membrane processes. However, a large fraction of the formed fouling can be easily removed by the large range of cleaning strategies available for the various membrane processes. These strategies include physical (i.e., relaxation,

backwashing for low-pressure systems) and chemical cleanings and are generally implemented in complement of fouling control methods (i.e., aeration in submerged systems, high feed cross flow velocities in pressurized membranes, etc.).

The degree of fouling reversibility is known to strongly depend on the frequency, duration, and strength of the cleaning method. As more energy and time are used during the cleaning episode, more foulants are expected to be removed from the membrane surface. It is also accepted that the rate of reversibility decreases with the time of cleaning, up to a point at which further cleaning does not remove a significant amount of foulant. This allows optimization of cleaning strategies for fouling reversibility. A reasonable trade-off between the maintenance costs due to cleaning and the loss of productivity due to decrease of hydraulic performances therefore remains a difficult task, and detailed cleaning strategies are generally provided by membrane suppliers.

Cross-References

- [Reversible Flux Decline](#)
- [Reversible Fouling Resistance](#)

Reversible Fouling for Constant Pressure Operation

► Reversible Flux Decline

Reversible Fouling Resistance

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Synonyms

Hydraulic resistance due to reversible fouling

The fouling propensity of a given feedwater can be quantified through the assessment of the additional hydraulic resistance resulting from the deposition of the fouling materials on the membrane surface. At the end of the filtration episode, the total hydraulic resistance (R_T) can be determined by using transmembrane pressure (TMP) and flux values, based on Darcy's law, as outlined in detail by Metzger et al. (2007). Specifically, the fouling resistance (R_F) can then be calculated by

subtracting the intrinsic membrane resistance (R_m) from R_T .

A method for advanced characterization of the fouling layer (and their relative resistance) was also proposed through a fragmentation method (Fig. 1, Henderson et al. 2010). In this method, the fouling layer was removed sequentially via a three-step cleaning procedure, whereby an increasing amount of strength was applied to detach the foulant layers from the membrane surface. This also helps to assess the preferential deposition of foulants on the membrane surface. Specifically, it is proposed to (1) rinse, (2) backwash, and (3) chemically clean the membrane, in that order. Operating details are provided in Henderson et al. (2010) for a small 0.01 m² hollow fiber modules. Upon removing each layer, a clean water test was undertaken to determine the residual resistance associated with the membrane (R_{Rinsed} , $R_{Backwashed}$, and $R_{Desorbed}$, respectively). Hence, the hydraulic resistance associated with each foulant layer (R_R , R_{BW} , R_D , and R_{IR} , respectively) was calculated using Eqs. 1, 2, 3, and 4.

$$R_R = R_T - R_{Rinsed} \quad (1)$$

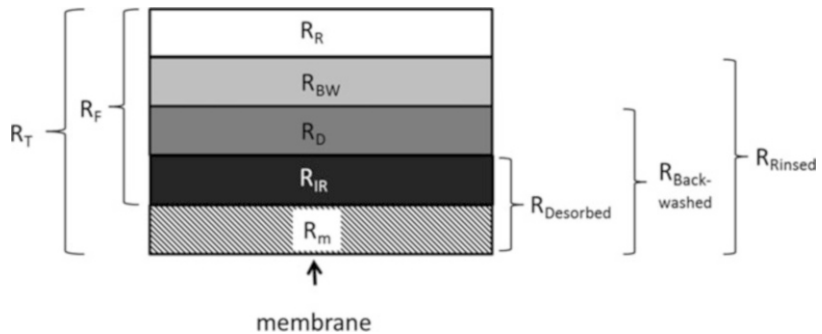
$$R_{BW} = R_{Rinsed} - R_{Backwashed} \quad (2)$$

$$R_D = R_{Backwashed} - R_{Desorbed} \quad (3)$$

$$R_{IR} = R_{Desorbed} - R_m \quad (4)$$

Reversible Fouling Resistance,

Fig. 1 Conceptual schematic of the hydraulic resistance recovered from the foulant layers on the membrane surface during various stages of cleaning (i.e., rinsing, backwashing, and chemical cleaning)



Cross-References

- [Physically Reversible Fouling](#)
- [Reversible Flux Decline](#)
- [Reversible Fouling](#)

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Rheology of Emulsions

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Rheology is the study of deformation and flow of matter. Rheological characterization is thus on the one hand important to control membrane processes because viscosity determines wall shear stresses at constant velocity profiles. On the other hand it can be used to investigate structure and stability of emulsions as well as for characterization of the product properties.

For the description of rheological properties it is most often distinguished between viscous and elastic properties. Viscosity is the common measure to describe viscous properties resulting from internal friction in a fluid exposed to an external flow field. The dynamic viscosity η is defined as the ratio between applied shear stress τ and resulting shear rate: $\eta = \frac{\tau}{\dot{\gamma}}$. The kinematic viscosity ν is the dynamic viscosity divided by the density of the fluid ρ :

$$\eta = \frac{\nu}{\rho}. \quad (1)$$

A fluid is called “Newtonian” if viscosity is independent of the applied shear rate. If viscosity increases with increasing shear rate, the fluid is called shear thickening or dilatant. A fluid showing decreasing viscosity with increasing shear rate is called shear thinning or pseudoplastic. Elasticity means that energy is stored in a fluid and released at a later point of time.

The rheological behavior of a fluid can be characterized using different kinds of viscometers and rheometers. Devices like u-tube and falling sphere viscometers can only be used to characterize Newtonian fluids. On the other hand, rheometers enable the application of different shear rates and thus allow for a more detailed characterization of rheological behavior. High viscous products are characterized in capillary rheometers. Here, the fluid is forced through a pipe and orifice with known dimensions. For emulsions, shear rheometers are most commonly used. They measure the torque which is required to deform a fluid with an applied shear rate or vice versa. Different measurement geometries are used for fluids with different properties. Low viscous fluids like aqueous solutions are most often measured using Couette cells. Fluids of higher viscosity are in general measured in cone-plate systems. In order to not destroy complex fluids like emulsions, plate-plate systems are used. Shear rheometers can either be used at constant shearing or in oscillatory mode. For oscillatory measurements a sinusoidal shear deformation is applied and the resulting stress response is recorded. This measurement allows for gaining information about viscous as well as elastic properties of fluids (Metzger 2006).

Rheological behavior of emulsions is strongly influenced by their composition as well as by their structure (Derkach 2009). Emulsions behave like suspensions with solid spheres as long as the applied shear rate is low enough and the drops are small enough not to be deformed during the measurement. This means that the viscosity of emulsions is strongly influenced by their dispersed phase content. The higher the volume of the drop phase, the higher is the viscosity. For low dispersed phase contents (DPC), the relationship between DPC and viscosity is linear and the fluids are Newtonian. For intermediate DPC,

shear-thinning flow behavior occurs because the drops interact with each other and form clusters. The relationship between DPC and relative viscosity η_r is expressed by different mathematical equations. The Krieger-Dougherty equation is used quite often. With intrinsic viscosity η_i and DPC at closest packing DPC_p (Krieger and Dougherty 1959):

$$\eta_r = \left(1 - \left\{\frac{DPC}{DPC_p}\right\}\right)^{\eta_i \times DPC_p} \quad (2)$$

In addition to DPC , drop size distribution influences the rheological behavior because it determines the closest packing of the spheres. If emulsion drops are deformed, they show elastic behavior. This can either be caused by dispersed phase contents higher than the closest packing or by shear rates high enough to deform the drops.

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Richardson Law

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The Richardson equation relates the permeation flux of hydrogen through dense membranes to the temperature, pressure difference, and membrane characteristics (Gallucci et al. 2007). In general, the hydrogen mass transfer mechanism through (Pd-based) membranes can be described by: (a) a traditional solution–diffusion mechanism for dense

membranes and (b) a Knudsen diffusion mechanism or combined mechanism of Knudsen diffusion and surface diffusion for porous membranes.

More in detail, the hydrogen permeation through a dense palladium layer is a complex process which consists of the following seven-step activated mechanism:

1. Mass transfer of hydrogen upstream toward the membrane surface and adsorption of hydrogen molecules on the membrane surface
2. Dissociation of hydrogen molecules on the same surface
3. Dissociation of the chemisorbed molecule into atomic form H^* consisting of a proton and an electron
4. Solution of the dissociated hydrogen atoms H^* into the lattice of the metal
5. Diffusion of the dissociated hydrogen atoms H^* through the lattice toward the downstream surface of the membrane
6. Recombination of H^* into hydrogen molecules H_2
7. Desorption of the H_2 molecules and mass transfer into the downstream bulk

For thick membranes, step 5 (diffusion of hydrogen atoms through the lattice) results in controlling the whole process. The diffusion of hydrogen atoms through the lattice can be described by the well-known Fick law:

$$J = D \frac{dc}{dx} \quad (1)$$

where J is the hydrogen flux through the lattice, D is the hydrogen diffusion coefficient, and c is the hydrogen concentration.

Under these conditions, the thermodynamic equilibrium between the hydrogen molecules in the gas phase and hydrogen atoms dissolved at the interface would be established and it can be described by

$$c = S \cdot p^n \quad (2)$$

where S is the hydrogen solubility and p the hydrogen partial pressure.

The hydrogen permeation at constant temperature through a dense palladium membrane is described by the following general expression:

$$J_{H_2} = P_{H_2} \frac{(P_{H_2, \text{upstream}}^n - P_{H_2, \text{downstream}}^n)}{t} \quad (3)$$

where J_{H_2} is the hydrogen flux through the membrane, P_{H_2} the hydrogen permeability, t the membrane thickness, p the hydrogen partial pressure, and n the dependence factor of the hydrogen flux on the hydrogen partial pressure, experimentally determined in the range 0.5–1 (Dittmeyer et al. 2001). When n is 0.5, the hydrogen flux follows the so-called Sieverts' law.

The hydrogen permeation through membranes is an activated process ruled by an Arrhenius law:

$$P_{H_2} = P_{H_2}^0 \exp\left(\frac{-Ea}{RT}\right) \quad (4)$$

where $P_{H_2}^0$, Ea , R , and T are the pre-exponential factor, the apparent activation energy, the universal gas constant, and the absolute temperature, respectively. Consequently, when n is 0.5, the hydrogen flux can be written in terms of the so-called Richardson equation:

$$J_{H_2} = P_{H_2}^0 \exp\left(\frac{-Ea}{RT}\right) \frac{(P_{H_2, \text{upstream}}^n - P_{H_2, \text{downstream}}^n)}{t}. \quad (5)$$

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Sanchez and Lacombe Theory

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This is a molecular theory for classical fluids, based on a compressible lattice fluid (LF) model for the representation of the microstates of pure components and mixtures. Each molecular species is considered decomposed in a sequence of contiguous segments (r-mers). The lattice cells are either empty or occupied by a molecular segment of the components in the mixture. The volume of the cells is allowed to vary with composition. Statistical arguments are used to calculate the number of configurations available for a system of N molecules with given configurational energy and volume; the partition function is calculated from statistical mechanics results as a function of temperature and pressure, in a mean field approximation, and finally, a simple expression for the total Gibbs free energy is obtained for pure species (Sanchez and Lacombe 1976) and for mixtures (Lacombe and Sanchez 1976). In the derivation, the flexibility parameter of the r-mers and the close-packed volume of a molecule are assumed independent of temperature and pressure.

Relevant results of the theory are represented by the expression of Gibbs free energy:

$$\frac{G}{rNRT^*} = -\tilde{\rho} + \frac{\tilde{p}}{\tilde{\rho}} + \tilde{T} \left[\left(\frac{1}{\tilde{\rho}} - 1 \right) \ln(1 - \tilde{\rho}) + \frac{1}{r} \ln(\tilde{\rho}) + \sum_i \frac{\phi_i}{r_i} \ln(\phi_i) \right] \quad (1)$$

and by the expression of the volumetric equation of state:

$$\tilde{\rho}^2 + \tilde{p} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r} \right) \tilde{\rho} \right] = 0 \quad (2)$$

Equation 1 has been written for the common case in which the number of configurations available for each r_i -mer in the close-packed pure state is unity. The quantities used by the model are defined in Table 1. The model expressions contain pure component parameters and one binary interaction parameter for each couple of components in the mixture.

The pure component parameters for a series of classical fluids are available (Sanchez and Lacombe 1976, 1978; Sanchez and Panayiotou 1994). The model can describe the liquid-vapor equilibrium conditions for pure components reasonably below the critical point (Sanchez and Lacombe 1976), as well as the phase equilibrium properties of different binary mixtures of simple classical fluids (Lacombe and Sanchez 1976), based on a single value of the binary interaction parameter; the latter value can be obtained from different experimental data for the mixture, i.e., from azeotropic temperature, change in volume or

Sanchez and Lacombe Theory, Table 1 List of symbols and properties used in the lattice fluid theory by Sanchez and Lacombe

	Symbol	Name	Definition/property
Pure component i	ρ_i^*	Characteristic density of pure component i	
	p_i^*	Characteristic pressure of pure component i	
	T_i^*	Characteristic temperature of pure component i	
	r_i^0	Number of lattice sites occupied by a mole of pure component i	$r_i^0 = \frac{M_i}{\rho_i^* v_i^*}$
	v_i^*	Volume occupied by a mole of lattice sites of pure substance	$v_i^* = \frac{RT_i^*}{p_i^*}$
	ε_i^*	Characteristic energy of pure component i	$\varepsilon_i^* = \frac{T_i^*}{k}$
Mixtures	N	Total number of moles	
	T	Temperature	
	p	Pressure	
	ρ	Density	
	ρ_i	Density of species i	$\rho_i = \omega_i \rho$
	ω_i	Mass fraction, $i=1,2,\dots,N_t$	$\omega_i = \frac{\rho_i}{\rho}$
	ϕ_i	Volume fraction	$\phi_i = \frac{\omega_i / \rho_i^*}{\sum_i \omega_i / \rho_i^*}$
	ρ^*	Characteristic density of the mixture	$\frac{1}{\rho^*} = \sum_i \frac{\omega_i}{\rho_i^*}$
	p^*	Characteristic pressure of the mixture	$p^* = \sum_i \phi_i p_i^* - \frac{1}{2} \sum_i \phi_i \sum_{j \neq i} \phi_j \cdot \Delta p_{ij}^*$
	Δp_{ij}^*	Binary parameter	$\Delta p_{ij}^* = p_i^* + p_j^* - 2(1 - k_{ij}) \sqrt{p_i^* \cdot p_j^*}$
	k_{ij}, Ψ_{ij}	Dimensionless binary parameter	$\Psi_{ij} = 1 - k_{ij}$
	r	Molar average number of lattice sites occupied by a molecule in the mixture	$r = \sum_i x_i r_i$
	T^*	Characteristic temperature of the mixture	$T^* = \frac{p^*}{r} \sum_i x_i r_i^0 \frac{T_i^*}{p_i^*} = \frac{p^* v^*}{R}$
	ε^*	Characteristic energy	$\varepsilon^* = \frac{T^*}{k}$
	v^*	Average close-packed mer molar volume in the mixture	$v^* = \frac{RT^*}{p^*}$
	$\tilde{\rho}$	Dimensionless density	$\tilde{\rho} = \frac{\rho}{\rho^*}$
	$\tilde{T}$	Dimensionless temperature	$\tilde{T} = \frac{T}{T^*}$
	$\tilde{p}$	Dimensionless pressure	$\tilde{p} = \frac{p}{p^*}$
		Volumetric equation of state	$\tilde{\rho}^2 + \tilde{p} + \tilde{T} [\ln(1 - \tilde{\rho}) + (1 - \frac{1}{r}) \tilde{\rho}] = 0$
	A	Total Helmholtz free energy	$\frac{A}{rNRT^*} = -\tilde{\rho} + \tilde{T} \left[\left(\frac{1}{\rho} - 1 \right) \ln(1 - \tilde{\rho}) + \frac{1}{r} \ln(\tilde{\rho}) + \sum_{i=1}^{N_t} \frac{\phi_i}{r_i} \ln(\phi_i) \right]$
	G	Total Gibbs free energy	$\frac{G}{rNRT^*} = -\tilde{\rho} + \frac{\tilde{p}}{\rho} + \tilde{T} \left[\left(\frac{1}{\rho} - 1 \right) \ln(1 - \tilde{\rho}) + \frac{1}{r} \ln(\tilde{\rho}) + \sum_{i=1}^{N_t} \frac{\phi_i}{r_i} \ln(\phi_i) \right]$

change in enthalpy upon mixing, mixture boiling point, UCST, and LCST (Lacombe and Sanchez 1976).

The model has been extended also to polymeric solutions (Sanchez and Lacombe 1978), considering that for the polymer species, the number of r-mers per molecule becomes infinitely large. The enthalpy of mixing of low molecular weight solutes in polymeric liquids may be well described by the model (Sanchez and Lacombe 1978). For polymeric mixtures the binary interaction parameters can be also reasonably predicted on the basis of the solubility parameters of the mixture constituents (Rodgers and Sanchez 1993). For its nature the model can describe well the equilibrium behavior of mixtures in the absence of strong polar interactions among the different components of the mixture.

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Sand Filter

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Introduction

Sand filters are employed as primary treatment in a water/wastewater industry. Raw water with various particle sizes of colloids need to be

coagulated/flocculated with coagulants and flocculants. The filter is filled with media such as garnet, sand of varying sizes, and anthracite. These filters could be dual-media or multimedia based on the raw water characteristics. A very high degree of clarity is achieved in the filtered water on account of finer particles of garnet at the bottom which trap finer turbidity particles. Turbidity is trapped and held throughout the entire bed depth, rather than the top 1 or 2 in.

Mechanical filtration will remove almost all forms of turbidity. In many cases, filters containing specially graded and sized gravel and sand are effective in screening out turbid particles. With such units, a periodic backwashing to remove the filtered material is all the maintenance necessary.

Zeta Potential: This is a commonly used term in filtration. An increase or decrease of zeta potential along with pH is an important criterion in particle adhesion during the filtration process. This is the scientific term for electrokinetic potential in a colloidal system. Its value is related to the stability of colloidal dispersions. It also indicates the degree of repulsion between adjacent similarly charged particles in a dispersion.

Filter Comparison

	Sand	Depth
Media	Single	Three
Bed usage	1–3 %	90 %
Service rate	2–4 gpm/ft ²	7–10 gpm/ft ²
Backwash	15 gpm/ft ²	15 gpm/ft ²
Removal	40 μ	10 μ

Types of Sand filter

Filtration is used in addition to regular coagulation and sedimentation for removal of solids from surface water or wastewater. This prepares the water for use as a portable boiler or cooling makeup. Filtration is a simple mechanical process involving mechanisms of adsorption (physical

and chemical), straining, sedimentation, interception, diffusion, and inertial compaction.

- Dual-media filter
- Multimedia filter

The sand in a pool sand filter (# 20 silica sand; 45–55 mm) is specially graded to trap particles in the 20–100 μ range. The size and shape of the filter media affect the efficiency of the solids removal. Sharp, angular media form large voids and remove less-than-rounded media of equivalent size. Though most suspended solids are trapped at the surface or in the first 1–2 in. of bed depth, some penetration is essential to prevent a sharp increase in pressure drop. As a sand filter collects dirt, its efficiency increases, trapping more dirt. The media need to be sufficiently coarse to allow solids to penetrate the bed for 2–4 in.. It is time to backwash the captured dirt out of the filter. They need the lowest maintenance of the three types of pool filters. You may need to open up the tank every 5 years or so. Sand filters are the easiest to operate and maintain. If your sand filter requires frequent backwashing every week or two, the sand bed may be “mothballed,” or it may be “channeled.” It may calcify with calcium deposits. A properly sized sand filter could go over 10 years between sand changes.

The major advantages of dual media filtration are higher rates and the longer runs.

Soft swim require annual cleaning of the filter sand to prevent it from “gumming up.” High amounts of bather oils can gum up a sand bed.

Types of Media

Quartz sand, silica sand, anthracite coal, garnet, magnetite, and other materials may be used as filtration media. Silica sand and anthracite are the most commonly used types (e.g., in filters following a hot process softener where the treated water is intended for boiler feed, anthracite is usually used).

The terms “multilayer,” “in-depth,” and “mixed media” apply to a type of filter bed which is graded by size and density. Coarse

media, often 0.6–1.0 mm (0.024–0.04 in.) are used for closely controlled coagulation and sedimentation. Coarse, less dense particles are at the top of the filter bed, and fine, denser particles are at the bottom. Downflow filtration allows deep, uniform penetration by particulate matter and permits high filtration rates and long service runs. Because small particles at the bottom are also more dense (less space between particles), they remain at the bottom. Even after high-rate backwashings, the layers remain in their proper location in the mixed media filter bed.

The table below lists four media used in multimedia filtration. The use of too many different media combinations causes severe backwashing difficulties. High wash rates expand the magnetite layer which might wash away the anthracite from the filter necessitating high wash water.

Media in multimedia filters:

Media	Effective size, mm(in.)	Specific gravity
Anthracite	0.7–1.7 (0.03–0.07)	1.4
Sand	0.3–0.7 (0.01–0.03)	2.6
Garnet	0.4–0.6 (0.016–0.024)	3.8
Magnetite	0.3–0.5 (0.01–0.02)	4.9

Slow Sand Filtration (SSF)

Slow sand filtration technology is especially ideal for small communities required to use filtration to comply with new regulations.

How SSF Works

Slow sand filtration relies on both physical and biological activity in controlling plant pathogens. The filter bed in SSF is constructed of a medium with high surface area colonized by suppressive microorganisms. The media also presents a physical barrier to the passage of spores of plant pathogens (Figs. 1 and 2).

Advantages of SSF:

- It is low-energy consuming process.
- Has great adaptability in components and applications. Maintenance is minimal.
- Systems can be built and installed by laymen.

- Costs of building and running significantly lower than other disinfection methods.

In Australia, chlorination/bromination processes are most widely used for water disinfection in nurseries. Chemical treatments have

proven effective when used carefully; however, they are relatively expensive and present safety issues to the handlers and the environment.

A disadvantage of the SSF is the large amount of land required, a consequence of the slow rates of water filtration that are possible, typically only 10 % or less of the rates that are possible in rapid filtration.



Sand Filter, Fig. 1 A typical sand filter configuration

Sand Specifications

Sand is characterized by the diameter of the individual sand grain (0.15–0.35 mm) and the effective size of the composite sand, ES or d10. d10 is defined as the sieve size in mm that permits passage of 10 % by weight of the sand. The uniformity coefficient (UC) of sand is defined as d_{60}/d_{10} . Effective size (ES) is such that approximately 10 % of the total grains by weight are smaller and 90 % are larger. ES is the minimum size of most of the particles. Uniformity is measured by comparison of effective size to the size at which 60 % of the grains by weight are smaller and 40 % are larger. This latter size, divided by the



Sand Filter, Fig. 2 A typical slow sand filter for water purification

ES, is called the uniformity coefficient – the smaller the UC, the more uniform the media particle size.

It is recommended to use fine-grade sand (0.15–0.35 mm), uniformity coefficient (UC) always <3, preferably <2 and be washed free of clay, loam, and organic matter. Fine particles will quickly clog the filters and frequent cleaning will be required. Sand that is not uniform will also settle in volume, reducing the porosity and slowing the passage of water.

Biological Activity

Microbial activity builds up very quickly in greenhouse nutrient solutions, and slow sand filters become active in biological suppression without any special inoculation. Safe drinking water is a high priority for people without main facilities.

Slow gravity sand filters remove bacteria and other small particles from drinking water, making it safe to drink. Sand filters cannot cope with heavy metals or other excessive pollutants. Their prime purpose is to remove bacteria and particles. If the source of raw water has a high level of contamination, locate a new one. Even spring water or very clean water is to be checked for undesirable contaminants. If the water contains sediment, it should be passed through an initial settling tank before it gets into the sand filter.

How the Filter Works

The water passes through the sand from top to bottom. Any larger suspended particles are left behind in the top layers of sand. Smaller particles of organic sediment left in the sand filter are eaten by bacteria and protozoans which “stick” in the layers of slime that form around the sand particles, and the clean water which passes through the filter is safe to drink. Provided that the grain size is around 0.1 mm in diameter, a sand filter can remove all fecal coliforms (bacteria that originate from feces) and virtually all viruses.

Conclusion

Sand filters serve as the major equipment of filtration in every area of daily use – from swimming pools to household and water treatment plants. This primary treatment shall reduce the load on subsequent pressure filtration. Best engineering practices are advocated in the design of sand filters and operation thereafter for clear water suitable for downstream hygienic use. Clarifier effluents of 2–10 NTU may be improved to 0.1–1.0 NTU by conventional sand filtration.

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 Manual of design for slow sand filtration
 The Davnor BioSand Water Filter

Saturated and Supersaturated Solutions

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A solution is saturated with respect to a given substance when the maximum solubility of the substance is reached. This is reflected by the solubility constant of the solution (Linke and Seidell 1965). For example, for the precipitation reaction:



The solubility is determined by the equilibrium constant of the reaction, K_{AB} :

$$K_{AB} = [A^{n+}][B^{n-}] \quad (2)$$

$$\text{or } \frac{[A^{n+}][B^{n-}]}{K_{AB}} = 1 \quad (3)$$

with $[A^{n+}]$ and $[B^{n-}]$ the activities of A and B, respectively. The logarithmic form of this equation is the stability index, SI:

$$SI = \log \frac{[A^{n+}][B^{n-}]}{K_{AB}} \quad (4)$$

When $SI = 0$, the solution is saturated. When $SI > 0$, there is an excess of AB (l) in the solution, and the solution is oversaturated. When $SI < 0$, the solution is undersaturated.

AB can be any species, and the stoichiometry can be more complex than in this simple example. The saturation point (or the equilibrium constant) depends on the temperature and pressure of solution and is different for each species.

When a solution is oversaturated, precipitation may occur. Nevertheless, kinetics also play a role: for homogeneous precipitation (in the absence of an external surface), an SI of 3–4 is to be applied in general, whereas for heterogeneous precipitation, an SI of 1–2 is needed.

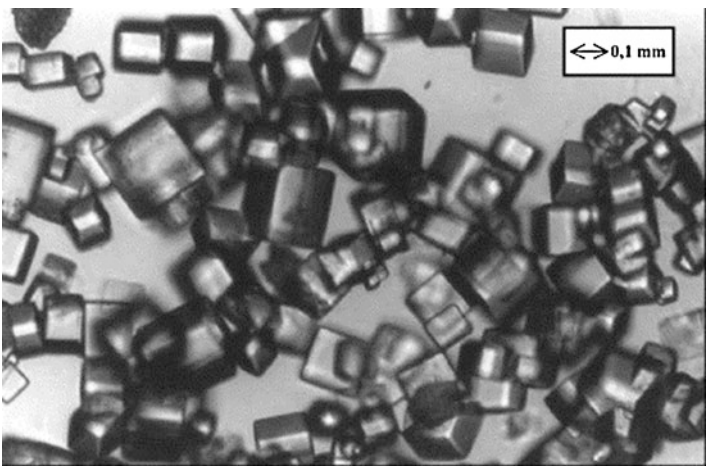
Precipitation of a supersaturated solution is important for membrane applications in two ways. First, the increase of the concentration of rejected species in the retentate may lead to oversaturation, depending on the initial concentration and the ratio of permeate to feed. These

species, typically salts, can subsequently precipitate on the membrane surface and block permeation; this phenomenon is referred to as scaling. Scaling leads to an increase in energy consumption and chemical cleaning frequency. The most well-known sparingly soluble salts are CaSO_4 and CaCO_3 (Pervov 1991), but other salts may also precipitate, such as BaSO_4 and phosphate and silica salts (Semiati et al. 2003, Chesters 2009). Solutions to prevent scaling include the use of antiscalants or acids such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). The use of acids is an effective solution, since the solubility of salts increases significantly at lower pH. Sulfuric acid is the most commonly used acid for this purpose.

Saturated and Supersaturated Solutions, Table 1 Pretreatment methods and their effect on scaling in reverse osmosis (Baker 2001) (XX highly effective, X moderately effective)

Pretreatment method	CaCO_3	CaSO_4	SiO_2
Acid dosage	XX		
Antiscalant dosage	X	XX	
Softening/ion exchange	XX	XX	
Preventive cleansing	X		X
Adjustment of process parameters		X	XX
Quick filtration			X
Flocculation			X
Micro- and ultrafiltration			XX
Candle filters			X

Saturated and Supersaturated Solutions, Fig. 1 High-purity NaCl salts obtained in a membrane crystallizer (Drioli et al. 2004, used with permission of Elsevier)



However, the trend is to use more hydrochloric acid, because sulfuric acid can negatively influence the fouling speed of a membrane by the addition of sulfate ions, which can stimulate precipitation of e.g., gypsum (CaSO_4).

A separate unit for removal of the scalant prior to the membrane separation might be necessary (Bremere et al. 1998), especially when going from high to very high feed recoveries (very high permeate to feed ratio). Some pretreatment methods and their effect on scaling are summarized in Table 1 (Baker 2001). However, a higher recovery shifts the problem to scaling of other salts with lower initial concentrations, which are not removed in advance. In any case, diagnosis, prediction, prevention, and control of scaling are important in any membrane application with scaling potential (Vrouwenvelder et al. 2003).

The membrane process in which the highest risk for scaling is encountered is reverse osmosis, because ions present in sparingly soluble salts are rejected by reverse osmosis membranes. Other processes related to salt removal or transport, such as electrodialysis and nanofiltration (and to a lesser extent, forward osmosis), are also at risk.

Supersaturation of salts is also crucial – and in this case a desired phenomenon – in the membrane crystallizers. It has been shown that in a membrane contactor producing supersaturated solutions, crystals with extremely high purity can be obtained, as shown in Fig. 1 for NaCl (Drioli et al. 2004). Similar results can be obtained for CaCO_3 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as solid products. Crystal growth generally starts at solute concentrations at which the nucleation occurs; the growth rate, depending on the supersaturation degree, is determined by a combination of the nature of the growing crystal surface and the diffusional rate (Curcio et al. 2001). Direct contact membrane distillation can be employed to reach the supersaturation required for crystallization.

Cross-References

- [Direct Contact Membrane Distillation \(DCMD\)](#)
- [Electrodialysis](#)
- [Forward Osmosis \(FO\)](#)

- [Membrane Contactor \(MC\)](#)
- [Nanofiltration](#)

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Scale Inhibitor

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Synonyms

Antiscalant

Introduction

Antiscalants (scale inhibitors) are used in drinking water and process industry to prevent scaling or scale deposits on the membrane surface in a membrane-operated water treatment plant. Scaling occurs when the solubility limit of sparingly soluble salts/minerals is reached leading to the salt precipitation on the membrane surface as the temperatures and pressures change. Scale inhibitors delay this process and allow higher concentrations of salts resulting in enhanced water recovery. Antiscalants are stable in process equipment and are slowly biodegradable in the receiving surface water.

What Is Scale?

Scale is a white chalky buildup of calcium minerals that occur as a result of the precipitation of normally soluble solids that become insoluble as temperature increases. Common examples of scale are calcium carbonate (CaCO_3), calcium sulfate (CaSO_4), barium sulfate (BaSO_4), and strontium sulfate (SrSO_4). Equally problematic are silica (SiO_2) and calcium fluoride (CaF) scales. Over time, without proper treatment, scale and other contaminants build up and reduce the flow. RO scale inhibitors eliminate scale and reduce fouling on the membranes, while specific scale inhibitors reduce corrosion on the boilers. The scale inhibitors prevent undesirable scale buildup on the equipments and affect the efficiency. Appropriate treatment by scale inhibitor, conforming to the source water chemistry, will extend the life of industrial equipment and provide optimal process condition.

Process Description

The chemical treatment of water associated with oil and gas includes the application of scale inhibitors – phosphonates – to help maintain the integrity of equipment used during the drilling and production phases. Treatment is used to reduce the concentration of scale-forming compounds. The accumulation of scale can reduce flow rates or lower the efficiencies in heat exchanger. The inhibitors can be applied downhole of the well-head and classified as:

- Oil miscible
- Totally water-free
- Emulsified and solid

Technical Capabilities

Available scale-inhibiting chemicals are effective at preventing mineral deposits caused by compounds such as CaCO_3 , SrSO_4 , CaSO_4 , BaSO_4 , FeS , and FeO . Appropriate scale inhibitor and dose will identify types and concentrations of scale-forming compounds in the water. Phosphonate-based scale inhibitors are effective in preventing carbonate and sulfate scales, whereas polymer base inhibitors are effective for sulfate/carbonate scales of barium, strontium, and calcium.

Reverse Osmosis (RO)

RO is a pressure-driven process, while its pretreatment being site specific is dictated by the raw water chemistry. Antiscalants reduce the extent of contaminants that attach to the membrane surface during operation. Primarily, they delay or retard the process of membrane fouling. Many antiscalants combat scaling and fouling by bonding with the contaminants in the water, thereby preventing it from attaching or sticking to the membrane surface. These contaminants are finally directed to the RO reject or drain.

A variety of antiscalants are available with varying chemistries based on phosphonates, phosphates, acrylates, maleic and carboxylic acids, and dendrimers. Selection of antiscalant is site and application specific; they have different capabilities for inhibiting scales that are encountered in RO system. Different antiscalant chemistries have unique mechanisms for slowing crystal growth. However, the antiscalants delay crystal formation by slowing induction time – *the time between nucleation (birth of a new crystal) and crystal growth*.

Three methods of scale control employed are:

- Acidification
- Ion exchange (zeolite) softening
- Antiscalant addition

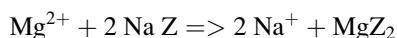
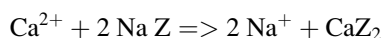
Acidification

Acid addition destroys carbonate ions, removing one of the reactants necessary for calcium

carbonate precipitation. This is very effective in preventing the precipitation of calcium carbonate while ineffective in preventing other types of scale. Disadvantages include corrosivity of the acid, the cost of tanks, monitoring equipment, and the fact that acid lowers the pH of the RO permeate.

Ion Exchange Softening

Sodium is utilized here which is exchanged for magnesium and calcium ions that are concentrated in the RO feed water:



(NaZ represents the sodium exchange resin)

When all the sodium ions have been replaced by calcium and magnesium, the resin is regenerated with brine. Ion exchange softening eliminates the need for continuous feed of either acid or antiscalant.

Threshold Inhibition

It is the ability of an antiscalant to keep supersaturated solutions of sparingly soluble salts. It prevents the precipitation of salts once the salt has exceeded its solubility product. The chemical inhibitors retard or delay the clustering process of charged ions and protonuclei. The most effective threshold inhibitors are based on phosphonic acids (or their salts) which have the added advantage of sequestering iron in a stoichiometric reaction. This is critical in membrane application as any soluble iron will cause rapid fouling while it oxidizes and becomes insoluble.

Performance

Antiscalant offers a variety of performance and application benefits. They are a powerful inhibitor tool against a variety of scales listed below.

CaCO ₃	CCPP >900 (LSI >2.8)
CaSO ₄	3.0 × K _{sp}
BaSO ₄	105 × K _{sp}
SrSO ₄	20 × K _{sp}
CaF	1,000 × K _{sp}
SiO ₂	120 ppm

The available antiscalants are highly effective at low dose rates in a wide range of feed water types and pH ranges. They provide both scale and inorganic fouling control while compatible with all membrane configuration and types.

CCPP: calcium carbonate precipitation potential. <http://www.awwa.org/Resources/RTW/CorrosivityCalc>

Saturation-level formulas for common scale-forming species

Calcium carbonate	(Ca)(CO ₃)/K _{sp} CaCO ₃
Barium carbonate	(Ba)(CO ₃)/K _{sp} BaCO ₃
Calcium sulfate	(Ca)(SO ₄)/K _{sp} CaSO ₄
Barium sulfate	(Ba) (SO ₄)/K _{sp} BaSO ₄
Amorphous silica	H ₄ SiO ₄ /(H ₂ O) ² × K _{sp} SiO ₂
Calcium fluoride	(Ca) (F) ² /K _{sp} CaF ₂
Strontium carbonate	(Sr)(CO ₃)/K _{sp} SrCO ₃
Strontium sulfate	(Sr) (SO ₄)/K _{sp} SrSO ₄
Magnesium hydroxide	(Mg) (OH) ² /K _{sp} Mg(OH) ²
Tricalcium phosphate	(Mg) (OH) ² /K _{sp} Mg(OH) ²

Material Safety Data Sheet (MSDS)

A Material Safety Data Sheet is a document that contains information on the potential hazards (health, fire, reactivity, and environmental) and how to work safely with the chemical product and an essential starting point for the development of a complete health and safety program. It also contains information on the use, storage, handling, and emergency procedures related to the hazards of the material. The MSDS contains much more information about the material than the label. MSDSs are prepared by the supplier or manufacturer of the material. It is intended to tell what the hazards of the product are, how to use the product safely, what to expect if the recommendations are not followed, what to do if accidents occur, how to recognize symptoms of overexposure, and what to do if such incidents occur.

The following categories of information must be present on the MSDS:

- Product information – product identifier (name), manufacturer and suppliers names, addresses, and emergency phone numbers
- Hazardous ingredients
- Physical data

- Fire or explosion hazard data
- Reactivity data: information on the chemical instability of a product and the substances it may react with
- Toxicological properties: health effects
- Preventive measures
- First aid measures
- Preparation information: who is responsible for preparation and date of preparing the MSDS

Scale Prediction and Saturation

Water is said to be saturated with a compound such as calcium carbonate if it will not precipitate the said compound or dissolve any of the solid phase of the compound when left undisturbed, under the same conditions, for an infinite period of time. Water that will not precipitate or dissolve a compound is at equilibrium for that compound.

The amount of a chemical compound that can be dissolved in water and remain in solution for this infinite period of time is described by the solubility product (K_{sp}). In the case of calcium carbonate, solubility product is defined by relationship:

$$(Ca)(CO_3) = K_{SP},$$

where (Ca) is the activity of sodium.

(CO_3) is the carbonate activity.

K_{SP} is the solubility product for calcium carbonate at the temperature.

In a more generalized sense, the term (Ca) (CO_3) can be called the ion activity product (IAP) and the equilibrium condition described by the relationship $IAP = K_{sp}$.

Scale indices developed are derived from the basic concept of saturation:

- If a water is undersaturated with a compound, $IAP < K_{sp}$. It will tend to dissolve the compound.
- If a water is supersaturated with a compound, $IAP > K_{sp}$. It tends to precipitate the compound.
- If a water is at equilibrium with a compound, $IAP = K_{sp}$. It tends not to dissolve or precipitate the compound.

Scale Inhibitor, Table 1 Antiscalant consumption

Consumption (kg/h) without second-pass brine recirculation	
First-pass RO	13.3
Second-pass front/rear	3.2/3.8
Total	20.3
Consumption with recirculation	
First pass	9.5
Second-pass front/rear	3.2/0.6
Total	13.3
Consumption in conventional RO design	
First pass	7.0
Second pass	7.0
Total	14.0

IAP = ion activity product; K_{sp} = solubility product.

Table 1 summarizes the overall results of antiscalant consumption at 300-ML/day of Adelaide (Southern Australia) Desalination Plant (ADP). It has been estimated that the antiscalant dose at this facility shall be 5 % lower than for a conventional RO design due to brine recirculation of the second pass ahead of the RO process.

Dosage Optimization

Induction time. Reactions do not occur instantaneously. A time delay occurs when all reactants are combined. They must come together in the reaction media to allow the reaction to occur. Thermodynamic evaluations of a water scale potential predict what will happen if water is allowed to sit undisturbed under the same conditions for an infinite period of time. Scale inhibitors do not prevent precipitation; they delay the inevitable by extending induction time (Ferguson 1984, Ferguson et al. 2011; Gill et al. 1983; Tomson et al. 2002; Amjad and Masler 1985).

Time selected is the residence time the inhibited water will be in the system. The inhibitor must prevent scale formation or growth until the water has passed through the system and been discharged.

Temperature affects the rate constant for the induction time relationship. As in any kinetic formula, the temperature has a great effect on reactants collision frequency. This effect is

independent of the effect of temperature on saturation-level calculations. A basic chemistry concept is that reaction rates increase with temperature. The rates approximately double for every 10 °C increase in temperature.

pH affects saturation level, but it also affects the dissociation state and stereochemistry of the inhibitors (Tomson et al. 2002). By virtue of its impact on the charge and shape of an inhibitor molecule, inhibitor effectiveness can be a function of *pH*, but may not always be significant in the *pH* range of interest (6.5–9.5). Acid dosage and consequently the *pH* of the medium have a significant bearing on the antiscalant dosage in a membrane-based treatment plant. Few BWRO (Brackish Water Reverse Osmosis) units can run without scale inhibitor.

Concentration Polarization

Concentration polarization is a phenomenon in which ion concentrations in a membrane's boundary layer are projected to be higher than those of the bulk water. The amount of boundary layer concentration can vary from 1.12 to 1.4 × that of the bulk water for clean membranes (Byrne 2002). Higher concentrations have been reported for fouled systems due to "cake-enhanced" concentration polarization.

Concentration polarization can affect all concentration-dependent calculations, including:

- *pH*
- Brine ion concentrations
- Recovery limits
- Maximum recovery based on antiscalant saturation-level maximum
- Dosage

Conclusion

Dosage models are available or can be developed for new inhibitors that allow accurate prediction of dosage requirements and treatment failure points. Specific scale inhibitors have been

developed for specific applications like for cooling systems, steam boiler systems, sulfamic acid-based descaler, corrosion nitrite inhibitor for chilled system, corrosion inhibitor (hard water) for open cooling systems, and air conditioning plant. Appropriate inhibitor is chosen after predicting the scaling tendency of the medium. Corrections in the modeling in high TDS brine are required as RO predictions lack accuracy due to use of simple indices. Such corrections are required for noncarbonate alkalinity and free ion concentrations. Scale inhibitor is an indispensable chemical in water and non-water segment. They aid in keeping the membranes from fouling so that the water will flow smoothly through. It is highlighted that appropriate selection or rather optimization of RO configuration can result in savings of up to 5 % as compared to conventional design.

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Screen Printing of Membranes

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Screen Printing

Screen printing is simple, economical, and versatile than traditional printing techniques. This technique is more suitable for flat or relatively flat surface; however, it could also work with less planar surfaces. A screen or fine mesh tightly stretched with a rigid frame is required. During printing, the undesired area of the mesh or screen is masked out according to the desired printing sketch. The screen is then positioned over the object to be printed and the ink is applied onto the screen followed by pressing the ink through the screen using squeegee. The distribution of masked and unmasked area of the screen design the print on the object followed by drying or curing. Proper postprint curing makes the print permanent and retains even under severe conditions. A variety of inks can be applied to a range of materials such as ceramics, textile, glass, metal, paper, and plastic. Consequently, screen printing is used in many industries including textile, medical devices, advertizing, snowboard graphics, decals, printed electronics, thick film technology, solar cells, fuel cells, membrane switches, etc.

Applications

Membrane Switches

Screen printing is commonly used in manufacturing process of membrane switches where circuit printing, graphic printing, and sometimes printing of industrial material such as adhesives and spacer layers can be achieved. Since membrane switches are used to enter function commands, they have wide range of applications in electronics such as

cellular phones, calculators, remote controls, machine controls, microwave ovens, and kitchen appliances, etc.

Screen printing offers a wide range of wet ink deposit thicknesses from which to create the circuits (from a few microns to several hundreds of microns). Moreover, printing of viscous conductive, resistive, and adhesive materials could be achieved. Inks used for membrane switches include polymer thick film silver conductive and resistive inks, adhesives, and solvent based (vacuum forming) and graphic UV-curing inks. Substrate materials typically used in membrane switch fabrication include polyester foils for the circuit layers and polycarbonate for the graphic overlays (Membrane Switches 2013).

Fuel Cell Membranes

Membrane electrode assembly (MEA) is an important part of fuel cells. Fabrication of MEA also involves the coating of catalyst layer onto membrane or to the gas diffusion layer. Catalyst layer structures can be modified by changing coating methods which significantly affect the performance of MEA. Spraying, screen printing, brushing, and decal methods have been applied to fabricate catalyst layers and carbon electrode layers to find out the economic ways suitable for mass production.

Spraying method and brushing method are widely used at laboratory scale but these methods are difficult to apply on large scale/mass production (Yoon et al. 2003). Sputtering is another interesting method for coating a small amount of catalyst in a vacuum, although it shows low single cell performance (Huang et al. 2006). The coating performed by decal method showed low electrochemical performance when applied to hydrocarbon polymer electrolyte membrane (PEM), which limits mass production and its application to various types of PEMs (Cho et al. 2009; Jeon et al. 2010). Owing to the advantages of reproducibility, easy procedures, and economic catalyst usage for mass production, the screen-printing method is proved as an efficient way to

coat the membranes with catalyst layer for fuel cells applications (Rajalakshmi and Dhathathreyan 2007).

Sensors

Sensors can also be fabricated by screen-printing technique. The chemical sensor consisting of transducer, sensitive membrane, and housing can be imagined as a system of layers. In such a planar potentiometric electrode, one layer can work as an electric contact of the electrode. The sensitive membrane can be the next layer, and finally the insulating layer that represents (together with the substrate) an equivalent of a conventional electrode body (Tymecki et al. 2006; Koncki et al. 1999).

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Secondary Growth Method

► Seeded Hydrothermal Synthesis for Zeolite Preparation

Secondary Growth Method for Zeolite Membrane Preparation

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Self-standing zeolite membranes are brittle and thus they are synthesized on porous supports to confer to the membrane mechanical resistance. The methods principally used for the zeolite membrane preparation are one-step (Vroon et al. 1998) and secondary growth (Lovallo et al. 1998). In the first one, the support is immersed in a suitable hydrothermal system and the membrane is synthesized under autogenous pressure. In this case, the membranes present defects due to the lack of connectivity between the crystals. In the secondary growth, the nucleation is decoupled from the crystal growth and so with the possibility to optimize the conditions of each state, independently. It presents two steps: seeding and growth. During the first phase, zeolite nanocrystals, prepared previously, are deposited on the support surface. In the second step, the seeded support is put in contact with a solution that favors the crystal growth by hydrothermal treatment. This method is more reproducible than the one step and at the same time permits to prepare thinner layer. In this method the very critical step is the seeding. In fact, if the seeded layer is sufficient uniform, the membrane is almost defect-free. However, the achievement of this result is not a very trivial task. The seeding procedures reported in literature (Lovallo et al. 1998; Kusakabe et al. 1999; Huang et al. 2004) permit to prepare membranes with

better permeation properties than those prepared with the one-step method. However, they present drawbacks that do not allow to prepare membranes' defect-free. Two of the most used are dip coating and rubbing. The first one, owing to the negative action of the gravitational force, leads to the formation of layer too rough and not very uniform (Hasegawa et al. 2002). In the rubbing (Kusakabe et al. 1999) small brushes are used to implant seeds on the support surface. It is not reproducible and the layer is not regular. More controllable seeding procedures involve the filtration of a zeolite water slurry through a porous support (Huang et al. 2004; Pera Titus et al. 2005). The cross-flow mode is the best way for obtaining a very thin layer because the zeolite slurry is pumped tangentially along the support surface. Using tubular support the layer is not uniform due to the negative action of the gravitational force. This disadvantage is overcome by combining the support tilting and rotation with the cross-flow filtration (Algieri et al. 2009). The slow rotation allows a crystals deposition on the whole membrane area. The tilting ensures the removal of bubbles air formed during the filtration and responsible of local defects.

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SEDE (Steric, Electric, and Dielectric Exclusion) Model: Approximated Versions

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DSP&DE Model: Approximated Versions

The DSP&DE model (known as the SEDE model in literature) is a transport model for nanofiltration (NF) which describes the separation properties as being the result of size effects, Donnan exclusion, and dielectric exclusion in terms of both Born dielectric effect and image forces contribution. The approximated versions of this model consider the dielectric exclusion (DE) in terms of only Born dielectric effect or only image forces.

DSP&DE (Image Forces) Model

Dielectric exclusion via image forces arises as a consequence of the difference between the dielectric constant of the membrane matrix (ϵ_m) and the dielectric constant of the solution in the nanopores (ϵ_p). Owing to the electrostatic effects resulting from the dielectric discontinuity, the ions in solution polarize the pore surface and interact with the polarization charges induced at the interface between the two dielectric media. The DE resulting from image forces has been extensively studied by Yaroshchuk (2000) who derived approximate expressions for the interaction energy in pores of cylindrical and slit-like geometries. These equations account for the screening of the interaction between the ion and the polarized interface by the membrane fixed charge and the ionic atmosphere as well.

The expression of the interaction energy $\Delta W_{i,im}^{int}$ (scaled on $k_B T$) for slit-like pores (which is mathematically less intense than that for cylindrical pores) takes the form:

$$\Delta W_{i,im}^{int} = -\alpha_i \ln \left[1 - \left(\frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + \varepsilon_m} \right) \exp(-2\mu^{int}) \right] \quad (1)$$

with

$$\alpha_i = \frac{(z_i F)^2}{8\pi\varepsilon_0\varepsilon_p R T N_A r_p} \quad (2)$$

and

$$\mu^{int} = \kappa r_p \sqrt{\frac{\bar{I}^{int}}{I^{int}}} \quad (3)$$

where z_i is the charge number of ion i , F is the Faraday constant, ε_0 is the vacuum permittivity, R is the ideal gas constant, T is the absolute temperature, N_A is the Avogadro number, r_p is the pore half-width, κ is the Debye parameter, and I is the ionic strength. The superscript int refers to a magnitude at the membrane/external solution interface and the bar to a magnitude inside the membrane. The parameter μ^{int} controls the screening of the interaction between the ion and the surface (via the image forces).

Some authors (Vezzani and Bandini 2002; Bandini and Vezzani 2003) assume that the role of the image forces is dominant as compared with the Born dielectric effect and neglect the variation of solvent dielectric properties in confined pores. ε_p in Eq. 1 is then replaced by the dielectric constant of the bulk solution (ε_b). This simplification is justified by the fact that the difference between ε_m and ε_b for most polymers is larger than the difference between ε_p and ε_b . In any case, the effects due to image forces are collected in the partition coefficients at the membrane/external solution interfaces, through energy terms ΔW_i .

As shown by Eqs. 1, 2, and 3:

- The transfer of an ion i from the external solution into a nanopore is unfavorable ($\Delta W_{i,im}^{int} > 0$) when $\varepsilon_p < \varepsilon_b$
- The magnitude of image forces is controlled by the square of the ion charge. Consequently, it does not differentiate (qualitatively) between co-ions and counterions (unlike the Donnan exclusion which repels co-ions but attracts counterions) and both co-ions and counterions are excluded from the membrane pores provided $\varepsilon_m < \varepsilon_p$.
- The magnitude of image forces decreases with increasing pore size. It should be noted that the magnitude of image forces strongly depends on the pore geometry, the dielectric exclusion in cylindrical pores being stronger than in slit-like ones (Yaroshchuk 2000)
- The screening of image forces is most relevant for concentrated solutions
- Unlike the Donnan effect, the Born dielectric effect exists even in the case of uncharged membranes.

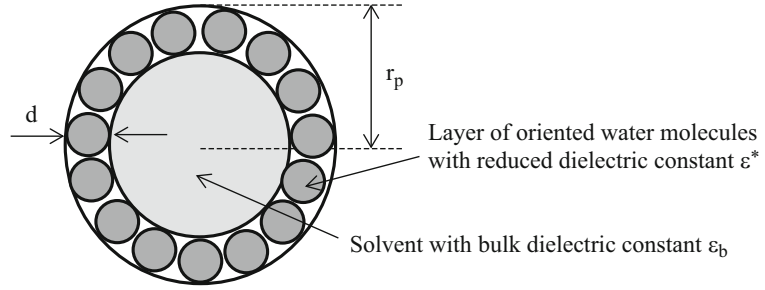
DSP&DE (Born Effect) Model

Some authors (Bowen and Welfoot 2002a, b) consider that due to the small pore size of NF membranes, ε_p approaches ε_m , reducing the effect of image forces. Therefore, this phenomenon is ruled out from their model and the Born DE is considered dominant.

The Born dielectric effect is due to the lowering of the dielectric constant of the solution inside pores (ε_p), with respect to the corresponding value in the external bulk solution (ε_b), which is caused by an alteration of the solvent structure when it is confined in nanodimensional pores. Indeed, the equilibrium and dynamical properties of a solvent in a confined geometry-like pores of NF membranes can differ significantly from those in the bulk (i.e., outside pores) because solvent molecules in such environments exhibit a greater degree of spatial and orientational order. This ordered structure reduces the ability of the solvent molecules to respond to an external electric field and, hence, leads to a decrease in the solvent dielectric constant. The reduction of dielectric constant means there is an energy barrier to solvation of ions into the pores (resulting in an ion

SEDE (Steric, Electric, and Dielectric Exclusion) Model: Approximated Versions,

Fig. 1 Schematic cross-section view of a cylindrical pore with ordered single layer of solvent at the pore surface and an inner annulus having bulk physical properties



partition at the interfaces between the membrane and external solutions), which can be estimated on the basis of the Born model (Born 1920) as:

$$\Delta W_{i, \text{Born}}^{\text{int}} = \frac{(z_i e)^2}{8\pi\epsilon_0 k_B T r_i} \left(\frac{1}{\epsilon_p} - \frac{1}{\epsilon_b} \right) \quad (4)$$

where z_i is the charge number of ion i , r_i is its radius, e is the elementary charge, ϵ_0 is the vacuum permittivity, k_B is the Boltzmann constant, and T is the absolute temperature. The ion radius (r_i) used in the original Born model is the bare ion radius. However, it is well documented that the Born model overestimates solvation enthalpies, especially for cations (Israelachvili 1991). Therefore, other ion radii as the Stokes radius (Bowen and Welfoot 2002a, b; Déon et al. 2009; Oatley et al. 2012) or the cavity radius (Szymczyk and Fievet 2005; Bouranene et al. 2009) are usually used in Eq. 4.

As shown by Eq. 4:

- The transfer of an ion i from the external solution into a nanopore is unfavorable ($\Delta W_{i, \text{Born}}^{\text{int}} > 0$) for any ion irrespective of the ion polarity (provided $\epsilon_p < \epsilon_b$)
- Multivalent ions are more strongly rejected than monovalent ones (provided $\epsilon_p < \epsilon_b$)
- The interaction is stronger for small ions
- Unlike the image forces, the Born effect does not depend on geometry and pore size
- Unlike the Donnan effect, the Born dielectric effect exists even in the case of uncharged membranes.

It must be stressed that the calculation of the excess solvation energy requires knowledge of ϵ_p

and, unfortunately, there is no independent direct measure of this quantity at the present time. Therefore, ϵ_p is used in most current NF models as no more than a fitting parameter to describe the ion rejection rates (Bowen and Welfoot 2002a, b; Bowen et al. 2004; Déon et al. 2009; Cavaco Morão et al. 2008; Bouranene et al. 2009; Oatley et al. 2012).

However, some authors (Bowen and Welfoot 2002a; Oatley et al. 2012) proposed a model for describing the solvent structure within the pores, in which the solvent is assumed to be consisted of a single layer of oriented water molecules at the pore surface and an inner part having bulk dielectric properties (Fig. 1). The variation of average pore dielectric constant can then be calculated on a geometric basis as:

$$\epsilon_p = 80 - 2(80 - \epsilon^*) \left(\frac{d}{r_p} \right) + (80 - \epsilon^*) \left(\frac{d}{r_p} \right)^2 \quad (5)$$

where ϵ^* is the dielectric constant of the single layer of oriented water molecules, 80 is the ϵ_b value, and d is the diameter of a water molecule (0.28 nm).

As shown by Eq. 5, the reduction of the dielectric constant ϵ_p originates only from confinement and does not depend on local ion environment, i.e., on type and concentration of ions. Moreover, the dielectric properties of the oriented solvent layer (ϵ^*) are expected to be controlled by the solvent-membrane interaction. Therefore, a stronger interaction, resulting, e.g., from a more strongly charged membrane, could lead to increased orientation and association and thus reduce ϵ^* . If ϵ^* is influenced by the fixed charges

on the pores and/or the membrane material (hydrophilic/hydrophobic, organic/inorganic...), then this parameter also becomes a fitting parameter. To date, the single oriented solvent layer approximation has not been sufficiently investigated to validate it.

Cross-References

- [Donnan Effect](#)
- [Nanofiltration](#)

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Seeded Hydrothermal Synthesis for Zeolite Preparation

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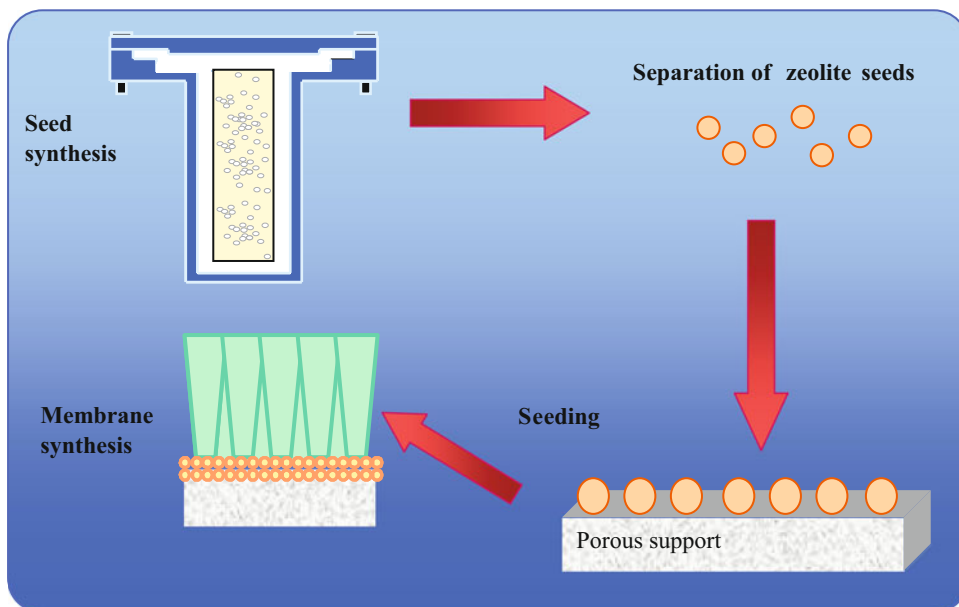
Synonyms

[Ex situ zeolite synthesis](#), [Secondary growth method](#)

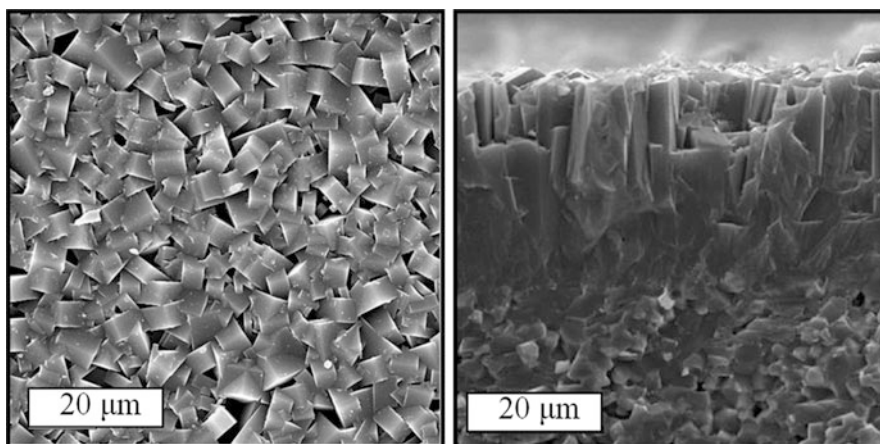
The hydrothermal synthesis procedures used to prepare zeolite membranes can be classified in two general groups: *ex situ* and *in situ* methods, that is with and without a previous seeding step. The secondary (seeded) growth method, decoupling nucleation and membrane growth, is considered as the most successful approach to control membrane formation (Caro et al. 2000; Arruebo et al. 2008).

This method includes a first step, seeding step, in which a closely packed layer of colloidal zeolite crystals, synthesized homogeneously, is deposited onto the surface of a support. These seeds, act as nuclei for further crystal growth with a secondary gel under hydrothermal synthesis conditions in the second stage, see Fig. 1.

The coating or seeding methods for zeolite membranes are dip coating, slip casting, rubbing, spray coating, laser ablation, spin coating, vacuum seeding, using of electrostatic forces, and covalent linkage. The attachment and bonding properties of the crystals on support depend on the chemical potential of the support to interact or react with the approaching zeolite crystal or crystal growth front. Because the concentration needed for secondary growth is lower than that



Seeded Hydrothermal Synthesis for Zeolite Preparation, Fig. 1 Scheme of the hydrothermal synthesis of zeolite membranes by separating the nucleation and the crystal growth steps



Seeded Hydrothermal Synthesis for Zeolite Preparation, Fig. 2 SEM analysis of silicalite membranes over nonporous alumina substrates after 20 h of secondary growth synthesis conditions. *Left*: top view. *Right*: cross section

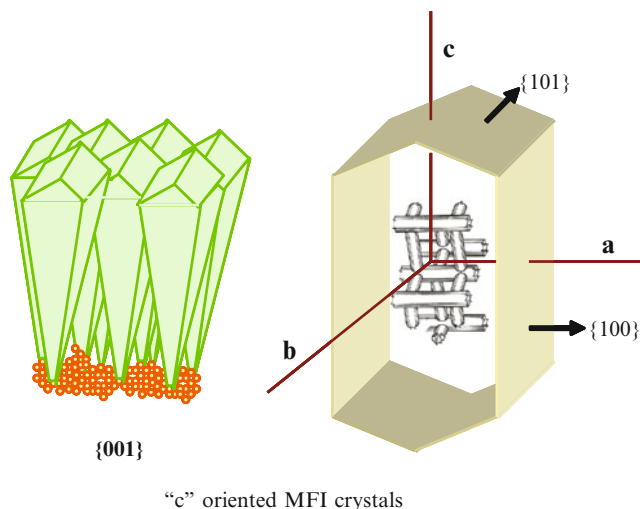
required for nucleation, further nucleation is strongly decreased and almost all of the crystal growth takes place over the existing crystal seeds. By controlling the composition and concentration of the secondary growth solution, the crystallization of undesired zeolite phases and the dissolution of the support can be avoided, and the rate

and direction of crystal growth can, to a certain extent, be controlled, see Fig. 2.

The aim of using the “ex situ” techniques is to obtain a better control of the microstructure and a preferential orientation of the crystals in the membrane with a shortened crystallization time. Preferential orientation is needed, not only for

Seeded Hydrothermal Synthesis for Zeolite Preparation,

Fig. 3 Schematic orientation of c-oriented MFI zeolite crystal



separation purposes when high fluxes are required, but also for size-selective chemical sensors. Due to the anisotropy in the pore geometry of the zeolite crystals, the orientation which shows the largest channels in the direction of the flux is preferable.

For example, on MFI zeolite, the straight and sinusoidal channels run parallel to the “b” and “c” axis respectively, see Fig. 3 Arruebo et al. 2008). The membranes prepared by secondary growth have rendered, in general, “c” oriented membranes, i.e., sinusoidal channels perpendicular to the support surface.

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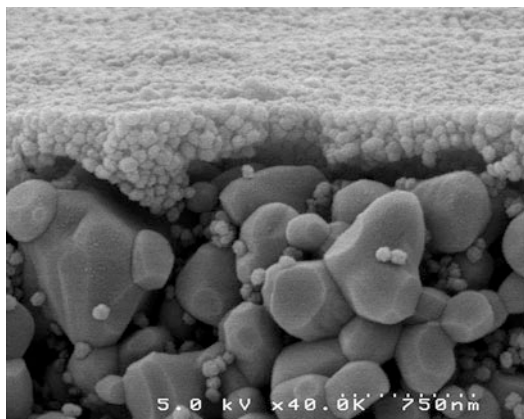
Seeding for Zeolite Membranes

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The seeding process can be described as a method in which a small piece of a single crystal/poly-crystal (seed) is used to act as an active site (nuclei) for growing a larger crystal when exposed to the effect of nutrients (liquids or gas) in a reaction system. The addition of seeds shifts the equilibrium toward crystal formation and avoids the undesirable random nature of spontaneous nucleation. This procedure is typically applied for solutions during recrystallization processes, thus eliminating the need for molecular collision/interaction and decreasing significantly the time required for nucleation. The seeding strategy is also largely applied for growing uniform zeolite membranes on porous supports, starting from a layer of closely packed seed crystals which have been previously nucleated (Julbe 2007). The decoupling of the nucleation step (at high supersaturation) from the crystal growth (at low supersaturation) makes the formation of a zeolite membrane very rapid as compared to direct growth without any seeds. As the concentration needed for secondary growth is lower than that for

Seeding

► Crystal Seeding



Seeding for Zeolite Membranes, Fig. 1 Layer of silicalite-1 (MFI) zeolite nanoseeds deposited by slip casting on a macroporous α - Al_2O_3 tubular support provided by Pall Exekia (Motuzas et al. 2006)

nucleation, further homogeneous nucleation is avoided and crystal growth occurs only on the existing seeds. Additional benefits include both the minimization or suppression of the crystallization of undesired phases and limitation of support dissolution (support etching might alter both its mechanical integrity and zeolite composition), while in some cases controlling the rate and direction of crystal growth. However, since the support is porous, uncontrolled infiltration of seeds in the pores might reduce membrane permeance by creating longer effective diffusion paths through the zeolite material (Hedlund et al. 2002). Controlled support seeding is therefore of great importance for growing uniform and good quality membranes, preferably with low infiltration into the porous support (Fig. 1). Classical coating or seeding methods are dip coating, slip casting, spin coating, rubbing, vacuum seeding, and spray coating. Specific methods for attaching zeolite seeds onto porous supports include either covalent linkage or electrostatic forces, using pH effects, cationic polymers, or silane coupling agents (Lai et al. 2004). Seeding with either commercial or homemade seeds is considered as one of the most attractive methods for preparing a variety of zeolite (e.g., LTA, MFI, SOD, FAU, CHA, DDR) and zeolite-type (e.g., MCM, MOF) membranes. It confers improved flexibility for controlling crystal growth and film

microstructure with high reproducibility and scalability. In industry, the seeding process is typically applied by Mitsui Engineering and Shipbuilding Co. Ltd. for the preparation of zeolite membranes, including LTA (Morigami et al. 2001).

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Segmented Block Copolymer

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Segmented block copolymers or multi-block copolymers with general formula $(AB)_n$ are linear macromolecules containing different rigid and flexible polymeric segment or block (Richard 2000). Usually, the flexible block has a glass transition temperature (T_g) below room temperature, whereas the rigid block has a glass transition temperature or melting temperature (T_m) distinctly higher (Holden et al. 2004). Microphase separation in the solid state derived from incompatible blocks is one of the most typical characteristic properties of segmented block copolymers (van der Schuur and Gaymans 2007).

The morphology depends on chemical compositions, chain structure, molecular weight of constituent blocks, thermodynamic interaction parameters, and used solvent during its process (Timothy 2003). They allow to extent significantly the property profiles of defined polymer materials by combining useful properties of two or more different prepolymers or polymers in one final product (Khastgir and Bhowmick 1998). The influence of the chemical structure and the chain length of segments upon the formation of “micro-domains” of the certain phase is very important and determines the final properties of polymer. Hence, at room temperature, these materials behave like elastomers, but at a temperature above T_g or T_m of the rigid block, the materials can be processed like thermoplastics (Richard 2000). Thus, these copolymers are considered as thermoplastic elastomeric materials, with several aspects of rubberlike behavior. Multi-block copolymers can be synthesized from different polymer segments having active functional groups at the chain end (Ebeling and Vana 2011). Basically, segmented block copolymers are formed in such a way that the chemical reaction employs both monomer and preformed functional terminated oligomers. Earlier, the segmented systems were synthesized through basic linkages involving isocyanate chemistry (Riegel and Kent 2003). In contrast to the segmented urethanes, amides, or urea copolymers, segmented polyester ether copolymers are generally prepared by the melt transesterification (Thomas et al. 2011).

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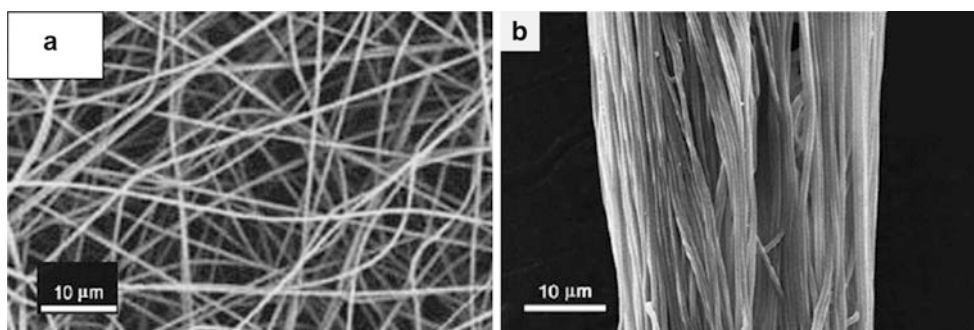
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Self-Bundling Electrospinning Method

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Self-bundling electrospinning is a technique used to induce alignment and self-bundling of electrospun nanofibers in the electrospinning process (Wang et al. 2008a). A typical electrospinning setup is employed in the self-bundling process, except that a grounded electrode (in the form of a needle tip which is used to induce the self-bundling of polymer nanofibers at the beginning of the electrospinning process) is inserted between the spinneret and the collection drum to alter the equal potential electric field lines between the spinneret and the collector. As a result, the shape of the equal electrostatic potential field lines has been changed. Then, the charged jet stream from the spinneret will be focused toward the tip of the inserted needle, promoting bundling of the formed electrospun fibers. The converged fibrous bundles could be wound around the drum to form a continuous self-bundling yarn. Empirically, the self-bundling has occurred when the conductivity of the polymer solution was higher than 10 $\mu\text{S}/\text{cm}$. Higher conductivity of the polymer solution than 400 $\mu\text{S}/\text{cm}$ could induce the self-bundling process simultaneously without using the grounded needle tip (Wang et al. 2008b). Moreover, by changing other parameters such as applied voltage, velocity of collection, solvent, polymer concentration, temperature, and humidity in the electrospinning process, the obtained electrospun nanofibers showed complex bundling structures.



Self-Bundling Electrospinning Method, Fig. 1 Representative electrospun nanofiber scaffolds with (a) typical and (b) self-bundling electrospinning methods (Wang et al. 2008a, b)

Self-bundled electrospun nanofibrous membrane exhibits unique mechanical properties as expected due to the aligned and bundled structure of the nanofibers and may be potentially useful in a variety of electrical, optical, mechanical, and biomedical applications. It should be noted that the production rate of the self-bundled nanofibers is relatively low at present; however, with the rapid development of multiple-jet electrospinning technology, this obstacle may be overcome (Fig. 1).

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Separation and Recovery of Gases, Multistage Process for

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Efficient separation of gases using membranes is dependent on several factors: The partial pressure of the gas to be recovered in the feed, the available

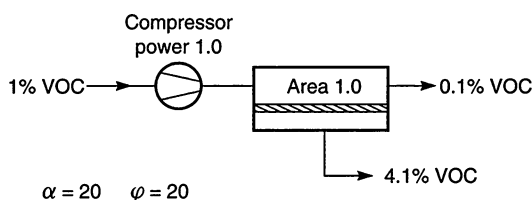
delta partial pressure over the membrane (feed - permeate), i.e., the driving force, the energy consumption needed for providing compression and/or vacuum, the purity demands for the product, and the value of the gas to be recovered. Typically increased driving force means increased flux and reduced membrane area, but at the same time increased energy consumption, hence there will be a trade-off between energy costs and capital costs. The type of flow patterns and flow velocities will also influence the efficiency of the separation – this has been nicely explained in the book of Geankoplis (2003).

Today the typical gas separation membrane process applications are hydrogen recovery from various types of gas streams (H_2 from synthesis gas, H_2 from refinery stream), oxygen–nitrogen separation for production of high purity N_2 - or O_2 -enriched air, CO_2 removal from natural gas (NG “sweetening”), upgrading of biogas (CO_2 - CH_4 separation), vapor gas separation (VOC recovery at oil terminals), and dehydration of air. The type of membrane materials used for the commercial processes today are relatively few, and they are polymers (cellulose acetates, polyimides, siloxanes). A dramatic increase in both new materials and applications is predicted (Baker 2012).

The separation taking place with the current polymer membranes is based on the solution-diffusion mechanism, and thus the difference in diffusion and solubility of the various gases in the membrane according to Eq. 1 expressing the flux of A through the membrane (J_A). In a gas mixture

the gases will be more or less nonideal, and the deviations from ideality are often more important than the difference in molecular size for the separation. Some of the new materials under development are using “carriers”; either fixed or mobile – this may add complexity to the process design, as the transport mechanism is now adding a second term to be considered (Eq. 2). Then finally, in precombustion separation of H_2 from CO_2 could possibly be performed using a palladium (Pd) membrane, by transporting H_2 as a proton (H^+) through the membrane; then the transport will basically follow Sieverts’ law (not discussed here):

$$J_A = \frac{P_A}{l} (p_h x_A - p_l y_A) \quad (1)$$



Separation and Recovery of Gases, Multistage Process for, Fig. 1 Recovery of volatile organic compounds (VOC) from air stream. Typically one-stage, highly permeable rubbery polymer (siloxane), but concentration in feed is usually low; hence, the concentration in the permeate will also be quite low even when 90 % have been removed (Baker 2012)

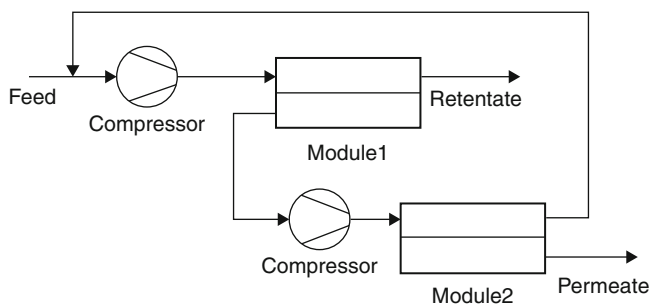
where P = permeability, l = thickness of membrane, Δp = driving force (in parenthesis)

$$J_A = \frac{P_A}{l} (p_h x_A - p_l y_A) + \frac{D_{AC}}{l} (c_{AC,0} - c_{AC,l}) \quad (2)$$

where the transport of the complexed compound AC is now added, D = diffusion coefficient, c = concentration.

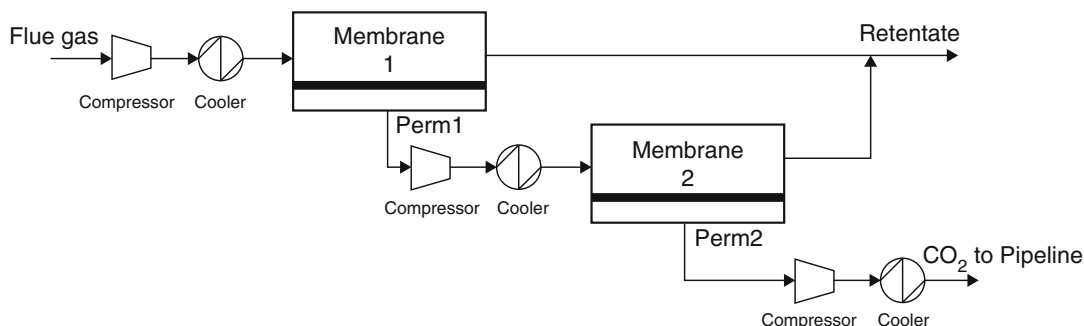
All these considerations mentioned above must be taken into account when the membrane separation process is being designed, and various types of multistage processes can be optimized for the most efficient and economical separation. Quite often a recycle of retentate or permeate streams is needed or uses of sweep gas on permeate side to increase the driving force over the membrane. It is quite complex to design the preferred separation process, and simulations are needed – it is therefore not only one solution. Several good examples are illustrated in the books of Baker (2012) and Mulder (1996) and likewise in publications of Favre (2007) and Hussain and Hägg (2009).

Several scenarios can be pictured depending on gases to be separated. Some examples are given (Figs. 1, 2, 3 and 4).



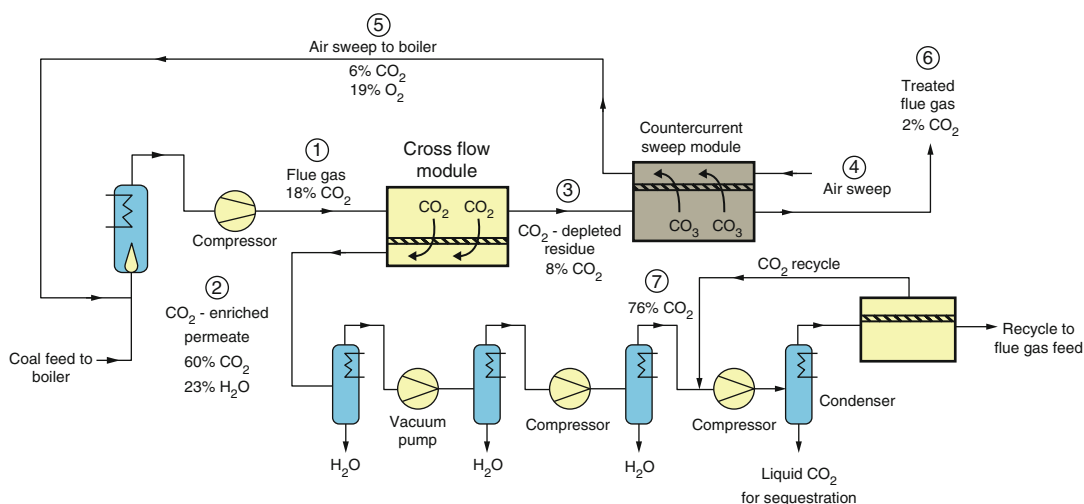
Separation and Recovery of Gases, Multistage Process for, Fig. 2 Upgrading of biogas, typically two stages with recycle for minimizing the CH_4 -loss and produce high purity CH_4 – in this case four designs were

compared, in the process shown, 99 % of the CH_4 were recovered from a water saturated biogas containing 65 % CH_4 and 35 % CO_2 (Deng and Hägg 2010)



Separation and Recovery of Gases, Multistage Process for, Fig. 3 Recovery of CO₂ from flue gas – large volume gas streams; combination of low feed pressure and vacuum on permeate side may be most

economical – illustrated for a facilitated transport membrane with 10 % CO₂ in flue gas (Hussain and Hägg 2010) with 90 % CO₂ capture and 90 % purity



Separation and Recovery of Gases, Multistage Process for, Fig. 4 Last but not least; smart process solutions – here for CO₂ capture from flue gas using a

high-flux, moderate selective membrane, and using air as sweep on the second stage which is then fed to the boiler (MTR-process) (Merkel et al. 2010)

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Separation of Organic from Organic Components (Pervaporation Application)

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Separation of organic-organic compounds is one of main areas in which pervaporation (PV) is employed together with solvent dehydration and removal of volatile organic compounds (VOCs) from aqueous solutions. Many organic compounds either have a close boiling point or they form azeotropic mixtures that cannot be efficiently separated by common techniques such as distillation. In this framework, pervaporation can be used to separate these mixtures alone or, most of the times, combined with distillation in a hybrid process in order to improve the separation efficiency.

Pervaporative organic-organic separation is the least developed field of application of pervaporation, and it is still very challenging principally due to the lack of membranes able to resist to the harsh conditions of solvents and the high temperatures required by the process (Baker 2004). In order to overcome the swelling effect and the degradation phenomenon caused by organic solvents, cross-linked membranes and blended polymeric materials have been developed and employed. On the other hand, inorganic and inorganic-polymer hybrid membranes gained a great acceptance, thanks to their high mechanical, thermal, and chemical stability.

The choice of using hydrophilic or hydrophobic membranes is based on the solubility of the target organic compound in a particular material.

With the installation of the first plant for the separation of methanol/methyl tert-butyl ether mixture in 1991, the commercial interest in the separation of organic mixtures through pervaporation started to rise. Over the last 50 years, organic pervaporation has been extensively investigated by the chemical and

petrochemical industries in which refinery streams contain a large number of organic components such as benzene, styrene, and toluene.

Pervaporative organic-organic separations can be classified as:

- (i) Separation of polar/nonpolar solvent mixtures such as methanol/methyl tert-butyl ether and ethanol/ethyl tert-butyl ether
- (ii) Separation of aromatic/aliphatic and aromatic/alicyclic mixtures such as benzene/cyclohexane
- (iii) Separation of aliphatic hydrocarbons such as toluene/isooctane
- (iv) Separation of isomers such as *m*-/*p*-xylene and *n*-/*t*-butanol (Smitha et al. 2004)

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Sequential Dilution Diafiltration

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Sequential dilution diafiltration is simply another name for discontinuous diafiltration by sequential dilution.

It involves repeated dilution of a solution followed by batch ultrafiltration. In the dilution step, both the macrosolute product and the microsolute impurity are reduced in concentration.

In the subsequent ultrafiltration step, in which the ► **retentate** volume is reduced to its original value, the macrosolute, which is assumed to have a rejection coefficient of 1.0, is increased in concentration to its original value, while the

concentration of microsolutes, whose rejection coefficient is zero, remains at its value *post*-dilution.

Sequential dilution diafiltration can be performed as a multistage process, leading to a reduction in buffer consumption for a given reduction in microsolutes concentration.

Serum Proteins

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Roughly 10 kg of milk consisting of 4 % fat, 2.6 % casein, and 0.7 % serum protein, but mostly of water (Walstra et al. 1999), is needed to produce 1 kg of cheese. The fat and casein are mainly incorporated in the cheese, while the serum proteins together with κ -casein and most of the water become the whey. As indicated in Table 1, the whey proteins are considerably smaller (3–6 nm) than the casein micelles which are typically 20–300 nm.

Serum protein was previously considered a by-product, but nowadays, serum proteins have considerable economic value due to their outstanding emulsification, gelling, and foaming

properties, either as a serum protein isolate or concentrate or as a specific protein. To preserve these special properties, in some cases the cheese process is started from a concentrated casein stream, while most of the serum proteins are separated and don't receive a heat treatment that can be detrimental to their functional properties. We discuss here separation of serum proteins from regular serum, separation of serum protein from casein during a casein concentration step, and isolation of specific proteins.

The salt concentration in serum is high, and therefore demineralization is needed. Nanofiltration has a great benefit over ion exchange and electrodialysis that it reduces energy consumption and the partly demineralized can be processed further into powders (van der Horst et al. 1995). When comparing various membranes (PSF/PVP, ZrO₂, ZrO₂/PSF), Doyen and coworkers (1996) concluded that the flux of the membranes is determined by the fouling layer and not the permeability of the membranes. Prevention of gel layer formation is a critical step and limits the concentration factors that can be reached.

Various authors have investigated concentration of casein either with ultrafiltration (all protein is in that case concentrated to reduce the liquid flow in the cheese production lines) or microfiltration, which allows for concentration of casein over serum protein. When focusing on this latter option, four studies are illustrative for what is possible, as shown in Table 2. The obtained process conditions were very comparable with the exception of the work of Krstic et al. (2002) who used turbulence promoters, but also did not reach high concentration factors. In general it can be said that for concentration of casein micelles, control over the membrane flux and related fouling are the most important factors to keep into account and that high concentration factors of up to 10 are feasible.

The individual serum proteins have many different applications, as have their hydrolysates that are known to contain bioactive components. Since hydrolysates are much smaller than the proteins, they can be easily removed through ultrafiltration. Separating the whole protein from a

Serum Proteins, Table 1 Concentrations and sizes of proteins present in milk (Walstra et al. 1999)

	Concentration in whole milk (g/l)	Average molecular size or weight
Total serum proteins	0.7	3–6 nm
α -Lactalbumin	0.12	14 kD
B-Lactoglobulin	0.32	18 kD
BSA	0.04	66 kD
Protease-peptone	0.08	4–40 kD
Immunoglobulins	0.08	150–900 kD
Lactoferrin	0.01	86 kD
Transferrin	0.01	76 kD
Others	0.04	

Serum Proteins, Table 2 Comparison of casein concentration processes

Membrane type and flux	Process conditions cross flow/ pressure	Concentration factor	Source
Ceraflo 0.22 μm ; $2.5 \cdot 10^{-5}$ m/s	6.9 m/s; 190 kPa	3	Pouliot et al. 1996
Membralox 0.2 μm $1.9 \cdot 10^{-5}$ m/s	7.2 m/s; 193 kPa	2	Vadi and Rizvi 2001
$1.3 \cdot 10^{-5}$ m/s		10	
CeraMem asymmetric 0.05 μm ; $3.1 \cdot 10^{-5}$ m/s	5.4 m/s; 138 kPa	2	Punidades and Rizvi 1998
Membralox 0.1 μm ; $9.7 \cdot 10^{-5}$ m/s	0.45 m/s; 34 kPa turbulence promoters	1	Krstic et al. 2002
$2.5 \cdot 10^{-4}$ m/s	12.5 m/s; 65 kPa		

mixture is still a challenge; α -lactalbumin may, for example, first be thermally aggregated, prior to membrane ultrafiltration; alternatively also adjustment of pH and salt concentration can be used to influence electrostatic and steric interaction and in this way enhance the selectivity of ultrafiltration as described in, e.g., Cheang and Zydny (2003).

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Shear Stress, Control Fouling with

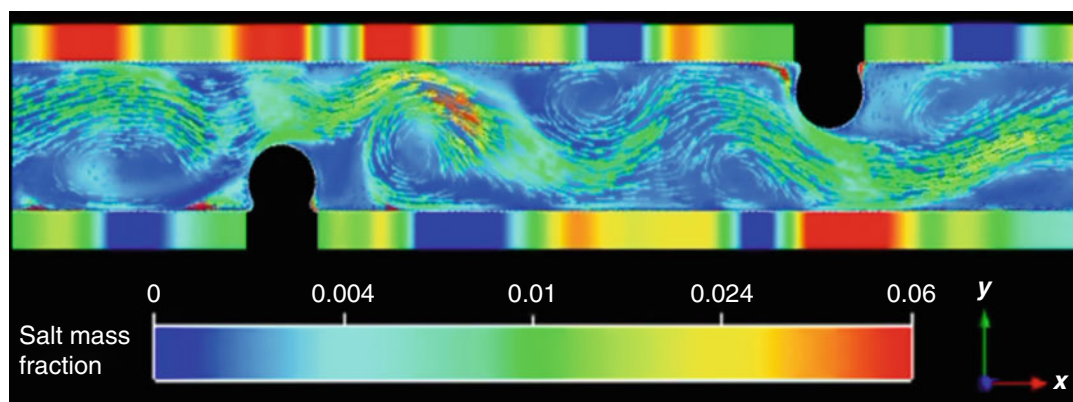
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One of the main strategies used to limit concentration polarization and fouling in membrane processes is to increase the shear stress in the vicinity of the membrane surface, so to enhance the mass transfer of foulants away from the separating interface. The deposition of particulate materials on membrane surface generally occurs when the local flux of a particle exceeds its critical value, which is strongly dependent on the characteristics of the particle and the overall operating conditions (i.e., hydrodynamics), affecting shear stress.

For example, high concentration of foulants results in increase in feed viscosity and, in turn, in decrease in the rate of diffusion coefficient to the feed (and the resulting Brownian back-diffusion) (Belfort et al. 1994). In addition, phenomena like shear-induced diffusion (i.e., migration of interacting retained particles in the direction of decreasing particle concentration) and inertial lift (i.e., motion of particles across a nonuniform shear field to an equilibrium position away from the channel wall) have also been described as back transport mechanisms provided by shear stress.

In biologically based membrane systems, like membrane bioreactors (MBRs), the transport,



Shear Stress, Control Fouling with, Fig. 1 Example of CFD modeling shear rate on membrane surface within spiral wound feed spacer (*top and bottom* colors: *red* is positive, *blue* is negative, and *green* is zero); inside colors

are salt concentration; *arrows* are sized and colored according to velocity magnitude (*red* is higher, *blue* is lower) (Picture supplied by Dr Gustavo Fimbres Weihs, UNSW, Australia)

adhesion, and bio-growth of bacterial cells are also strongly impacted by shear stress (Cui et al. 2003). Detachment of the biofilm results from interfacial transfer process, with diffusing cells from the biofilm back to the bulk liquid. As expected, biofilm detachment is observed to increase with both fluid shear stress and biofilm mass. However, other factors such as the limited availability of nutrients can also increase rate of biofilm detachment.

Implementation of High Shear Stress

In conventional pressure-driven membrane systems, the implementation of high shear stress is generally delivered through elevated flow rate of the feed stream and the use of feed spacers, increasing turbulence on the membrane surface.

Air scouring is generally used to control fouling in MBRs, and the effects of the two-phase flows circulating on the membrane surface have been extensively reviewed (Cui et al. 2003). In the case of hollow fiber MBR, aeration also results in fiber movement, which limits the deposition of materials on their surface. It is now generally accepted that, once a certain airflow rate is exceeded, no further significant fouling limitation is observed. Although few studies have indicated the greater performances obtained with small-size

bubbles, the large majority of the literature acknowledges that large bubbles create relatively more turbulence and, therefore, present a better option for antifouling strategy (Böhm et al. 2012).

Characterization of Shear Stress

Precise characterization of the shear stress in real membrane configurations is challenging and is generally limited to academic studies. Many research groups have developed elaborated computerized fluid dynamic (CFD) models to describe shear stress at micro- and macroscales. CFD studies have also been widely used to better describe flow patterns in narrow spacer-filled channels, like in spiral wound configurations generally found in reverse osmosis. These works have generally resulted into optimization of spacer geometric parameters and into better characterization of mechanisms responsible for mass transfer enhancement (Fig. 1). While two-dimensional (2D) flow models have been studied for a couple of decades, 3D solutions are also slowly emerging (Fimbres-Weihs and Wiley 2010).

However, in order to estimate shear forces in their membrane systems, practitioners tend to rely on simpler parameters, such as estimated cross flow velocities, Reynolds numbers calculated from bulk parameters like liquid flow rates

(obtained from pumping equipment), and dimensions of membrane vessels or modules. However, only very rough estimation can be obtained, with little opportunity to truly optimize and/or better understand their membrane operations.

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- membrane, (b) dissociation of the gas molecules on the surface of membrane, (c) dissolution of gas atoms into the metal bulk, (d) diffusion of gas atoms through the metallic layer, (e) association of gas atoms at the other side of the membrane, (f) desorption of the gas molecule from the surface of the membrane, and (g) external diffusion of the gas molecule to the gas bulk (Gallucci et al. 2013).
- In general the permeation of H_2 molecules through a Pd-based membrane (Basile and Gallucci 2009) follows:

$$J_{H_2} = \frac{P}{L} \left(P_{H_2, \text{retentate}}^{n_m} - P_{H_2, \text{permeate}}^{n_m} \right)$$

where J_{H_2} is the flux of H_2 through the membrane, P is the permeability of the membrane, L is the thickness of the metallic selective layer (Pd layer), $P_{H_2, \text{permeate}}$ is the partial pressure of hydrogen in the permeate side (the side that contains the permeated gas with lower pressure) and $P_{H_2, \text{retentate}}$ partial pressure of H_2 in the retentate side (the retained gas stream with higher pressure), and n_m is an exponent that depends on the rate-limiting step in the permeation phenomenon. At the presence of a thick selective metallic layer (Pd layer), diffusion of the gas atoms through this layer is the rate-limiting step, and n_m value will approach to 0.5. The reason is that the diffusion rate through the metal is proportional to the concentrations of H atoms on opposite sides of the membrane and this concentration is proportional to the square root of H_2 in permeate and retentate sides. In this case, the flux can be described by Sieverts' law (Yun and Oyama 2011).

In case of very thin selective layer (supported membranes with high fluxes), external mass transfer limitation (steps a and e) could be a limiting step (Tiemersma et al. 2006; Caravella et al. 2009). In this case, the value of n_m exponent will approach to 1. The reason is that in this case the permeation through the membrane will be proportional to the concentration of molecular hydrogen. At the presence of high flux through the membrane, the concentration of H_2 molecules close to the membrane will be lower than the value in the bulk of the flow. This phenomenon is generally named as concentration polarization

Sieverts' Law

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Adolf Sieverts (1874–1947) published an article in 1929 discussing the absorption of gases by metals and proposing a rule to describe this phenomenon (Sieverts 1929). According to Sieverts' law, the solubility of diatomic gases (such as H_2 , N_2 , and O_2) in metals is proportional to the square root of the partial pressure of the gas in thermodynamic equilibrium (Gupta 2003). In membrane science, the Sieverts' law is widely used to describe the permeation of H_2 through dense metallic (Pd-based) membranes via a solution-diffusion mechanism (Basile and Gallucci 2009). In general the transport of the gas (H_2) molecules from a high-pressure region to a low-pressure region follows several steps: (a) external diffusion of the gas molecules to the surface of the

which will result in lower performance of the membrane. n_m values greater than 0.5 might happen also in case of a tick defected membrane (pinholes on the surface of the membrane) where other permeation mechanisms as Knudsen diffusion or Poiseuille flow will play a role. In general the value for n_m should be measured experimentally with a defect-free membrane (Caravella et al. 2010).

Impurities (such as CO) in the feed gas stream can also deteriorate the performance of the membrane. This will result in lower permeation of H₂ through the membrane at the presence of certain amount of CO and will determine deviations from the Sieverts' law. Increasing the temperature will result in lower effect of CO on the permeation through the membrane (Scura et al. 2008).

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Silica DDR Membrane

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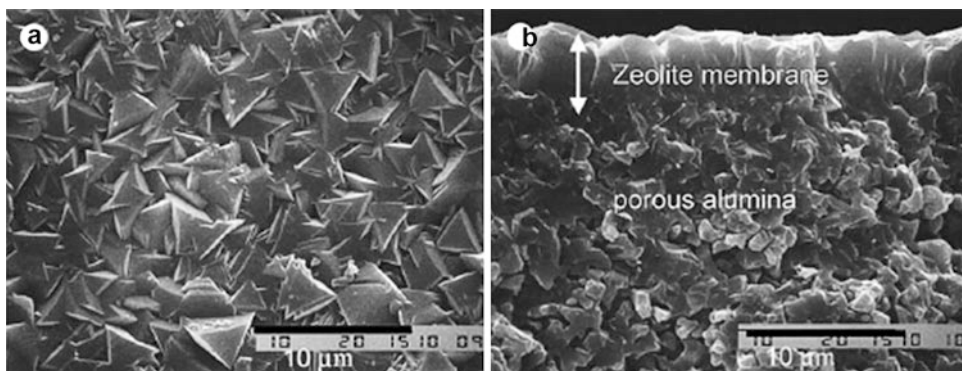
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Zeolite is an aluminosilicate mineral and possesses different crystal structures that determine the pore diameters, which vary between 0.3 and 1 nm (Hedlund 1998). Cavities and pores are uniform in size within a specific zeolite material and permit only molecules of certain size and shape to penetrate inside the channels and reject those of larger dimensions. This type of separation is termed as molecular sieving. Therefore, small-pore 8-ring window zeolites were developed for the separation of light gases. An example of such zeolite is all-silica decadodecasil 3 rhombohedral (DDR) with a window opening of 0.36×0.44 nm (Gies 1986). The topology of all-silica DDR consists of window-connected cages in the absence of aluminum, in contrast to zeolite frameworks, which makes this material a member of the group of clathrasils. Clathrasils are all-silica clathrate compounds with three-dimensional frameworks built of $[\text{SiO}_4]^{4-}$ tetrahedral linked in the corners with cage-like voids in between (Zhu et al. 2000). All-silica DDR can be considered as a link between zeolites and clathrasils because it possesses zeolitic properties through a clathrasil structure. The chemical composition of all-silica DDR can be represented as $[(\text{C}_{10}\text{H}_{17}\text{N})_6(\text{N}_2)_9][\text{Si}_{120}\text{O}_{240}]$, where $\text{C}_{10}\text{H}_{17}\text{N}$ is 1-aminoadamantane used as a template molecule in the synthesis.

The preparation of all-silica DDR membranes have been widely reported (Tomita et al. 2004; Bergh et al. 2008; Kuhn et al. 2008). As a general



Silica DDR Membrane, Fig. 1 SEM images of the microstructure of a DDR type zeolite membrane formed on a porous alumina substrate, (a) surface and (b) cross-

section (Tomita et al. 2004). Reprinted with permission from ref. Tomita et al. 2004. Copyright 2016, Elsevier

procedure of synthesis, all-silica DDR seed crystals are initially deposited on the surface of porous alumina substrate prior to the immersion in mixture solution of 1-aminoadamantane agent to grow a continuous DDR membrane and followed by the calcination process at high temperature ($\sim 700^\circ\text{C}$). The general microstructures of the resulted all-silica membrane are shown in Fig. 1. This figure indicated that dense all-silica DDR membrane was formed uniformly and the thickness of the membrane was 5–10 μm . The porous alumina substrate was commonly used as a support to provide high mechanical strength and low flow resistance to the membrane.

According to Bergh et al. (2008), the permeation and separation characteristics of light gases through all-silica membranes can be explained by taking into account three factors, which are (1) steric effects introduced by the window opening of all-silica DDR leading to molecular sieving and activated transport, (2) competitive adsorption effects, and (3) interaction between diffusing molecules in the cages of the zeolite.

Pore dimension of 0.36×0.44 nm allowed the all-silica DDR membrane to be very suitable for the separation of CO_2 and CH_4 , which have kinetic diameters of 0.33 and 0.38 nm, respectively. As reported by Tomita et al. (2004), the separation factor (SF) of CO_2 to CH_4 in 50 % CO_2 and 50 % CH_4 mixed gas feed for the synthesized all-silica membrane was in the range of 100–220 at 0.5 MPa total gas feed pressure,

which is much higher than that of other types of zeolite membranes such as FAU-type zeolite membrane (SF 20) (Kusakabe et al. 1997), MFI-type zeolite membrane (SF 16) (Lovallo et al. 1998), SAPO-34-type zeolite membrane (SF 30) (Poshusta et al. 2001), and LTA-type zeolite membrane (SF 0.5) (Aoki et al. 1998). Apart from its high potential in CO_2/CH_4 separation application, all-silica DDR membranes are also a good candidate for the separation of nitrogen/methane (SF 20–45), carbon dioxide and nitrous oxide/air (SF 20–400), and air/krypton (SF 5–10) (Bergh et al. 2008).

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Silica Gel for Membrane Preparation

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Silica Gel for Membrane Preparation

Silica gel is composed of silicon oxide manufactured widely for moisture removal. It is typically in solid form and possesses high ability in water absorption. The used silica gel can be regenerated by heat treatment at temperature range of 100–120 °C for several hours. In

addition, it is also a stable material, nontoxic, and easily available and inexpensive. Commercial silica gel typically has high surface area, large total pore volume, and broad pore size distribution (Wang et al. 2012). These characteristics produce less resistance for gas/liquid to diffusion into it and thus make this material potentially to be used as a membrane material.

Silica gel can be prepared via a chemical reaction between sodium silicate with an acidic solution at constant pH (Greenwood and Earnshaw 1997). To produce silica gel for commercial uses, a gelatinous precipitate obtained from the reaction is washed prior to the dehydration process to produce colorless silica gel. Typically, cobalt chloride or ammonium tetrachlorocobaltate is added to silica gel to give a visible indication of its moisture content (Greenwood and Earnshaw 1997).

However, for membrane fabrication process, silica gel can be synthesized using polycondensation of hydrolyzed tetraethoxysilane (TEOS) under acidic conditions through a sol-gel approach (Lavorgna et al. 2007; Mishra et al. 2012). This method is more favorable because high-purity silicate glasses can be obtained. Similar to other ceramic material, silica gel has hydroxyl group on its outer surface which enables anchoring process to be carried out effectively. This process is also known as functionalization which is a crucial step in the fabrication of membrane on the top of silica gel support which facilitates the intimidation between these two layers.

Various organic chemicals are used to functionalize silica gel, and the method to obtain chemical bridge between support and membrane might be different among research group. However, there is a general consensus in the way of functionalizing silica gel such as removal of moisture prior to functionalization process, stirring and mixing process between precursor of chemical bridge and silica gel, and washing and drying cycle using alcohol (Lavorgna et al. 2007). These preparation steps are rather simple without the necessity of using complex methods and advance equipments.

Silica gel has been recognized as a promising additive material in polymeric membrane for fuel cell application (Mishra et al. 2012). Due to its

high hydrophilicity in nature, it has been used to increase proton conductivity of commercial fuel cell electrolyte membrane, i.e., Nafion[®], and retain humidity when the membrane is used at temperature higher than 80 °C (Mishra et al. 2012). The incorporation of silica gel into polymeric membrane can be accomplished by adding the silica gel into polymeric solution prior to the casting step and the drying process (Mishra et al. 2012; Seo et al. 2006). This approach enables the silica gel to be homogeneously dispersed across polymer matrix. However, the functionalization of silica gel should be carried out prior to this process. On the other hand, the silica-based composite membrane can be fabricated by impregnation process (Mishra et al. 2012; Mahreni et al. 2009). This can be achieved by soaking the membrane by silica sol followed by functionalization process. These two approaches can be categorized as *ex situ* approach in producing composite membrane for fuel cell application. There is another approach known as *in situ* technique which involves the incorporation of either nanoparticles or their precursors into monomer solution with low viscosity (Mishra et al. 2012). This approach ensures better dispersion and physical properties but very little information can be obtained from open literature (Mishra et al. 2012). It is perhaps that this technique is rather scarce compared to *ex situ* approach. Furthermore, the incorporation of hydrophilic silica gel with a monomer obscures polymerization process causing a reduction in membrane molecular weight and the formation of undesirable cross-linking (Mishra et al. 2012). Therefore, the fabrication of commercial composite membrane for fuel cell application such as Nafion[®] uses an *ex situ* approach due to its simplicity and controllability.

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Silica Membrane

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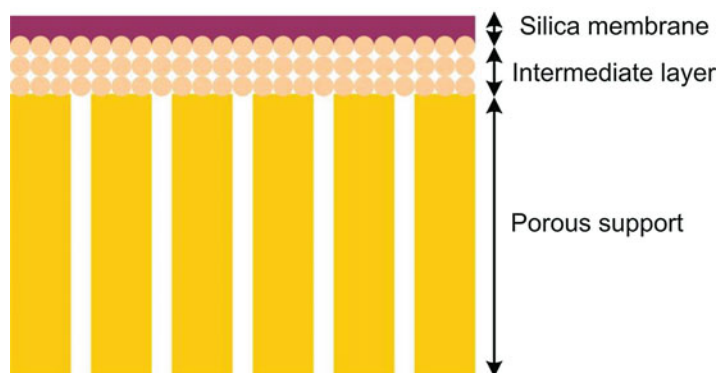
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Silica membrane is a thin layer of silicon oxide consisting of microporous structure with pore size distribution of 0.3 nm (Lee et al. 2011). This feature enables small molecules such as hydrogen to pass through its microporous channels. Silica membrane is robust to be used at higher temperature and harsh conditions for longer operating period due to high melting point of silica. However, silica membrane will suffer an instability problem if it is used at higher temperature in the presence of water vapor due to the densification of silica (Saito et al. 2012). However, this problem

Silica Membrane,

Fig. 1 Silica membrane is normally grown on an intermediate layer to produce defect free-membrane



does not occur when silica membrane is used at lower temperature.

To enhance the performance of silica membrane, the membrane should be fabricated as thin as possible to reduce the pressure drop; thus, it requires a porous support to enhance its mechanical stability (Kumar and Gulians 2010). Figure 1 shows the alumina support with high porosity is used to maintain the structure of silica membrane. Prior to the growth of silica membrane, an intermediate layer is fabricated on top of the porous support to ensure a uniform intermediate layer can be provided. This approach is to avoid the formation of crack or pinhole that reduces silica performance.

Sol-gel method is the most common approach used for the fabricating silica membrane of a porous support due to its simplicity, controllability, and homogeneity (Koutsonikolas et al. 2011). However, this technique is unreliable to produce a defect-free membrane. On the other hand, chemical vapor deposition (CVD) is an alternative method to synthesize silica membrane on a porous support, but it tends to produce a silica membrane with high selectivity but lower permeance (Koutsonikolas et al. 2010). In the fabrication process, a method to enhance the durability toward water vapor should be emphasized when considering the silica membrane for practical uses (Saito et al. 2012). To enhance the durability of silica membrane, an additive can be used which is added at the beginning of preparation step (Lin et al. 2012; Tseng et al. 2011; Wang and Tsuru 2011; Araki et al. 2011). The silica-composite membrane has been tested and the results showed

that the composite membrane possesses stability when operated under hydrothermal conditions (Yang and Chen 2011). Another method to enhance the stability of silica membrane is through the incorporation and carbonization of covalently bonded templates into silica matrix (Lin et al. 2012; Vos et al. 1999). This approach limits the movement of silica in its matrix, thus improving hydrostability of the membrane.

Silica membrane has an advantage to be used for hydrogen purification process compared to palladium in terms of its economic point of view (Oda et al. 2010). The common application that uses silica membrane is a membrane reactor for hydrogen separation. Silica membrane is used to separate hydrogen from reaction zone, thus facilitating the equilibrium conversion toward product formation, which gives benefit to the performance of the membrane reactor. Silica membrane with higher selectivity and permeability can be used in other applications that require membrane reactor such as water-gas shift reaction, ethanol steam reforming, Haber process, and methane reforming.

Silica membrane has also been potentially employed for various chemical processes such as desalination process and pervaporation (Lin et al. 2012). In desalination process, the separation of salt from water is made based on small kinetic diameter of water which is 2.6 Å compared to Na^+ and Cl^- , which are 7.2 Å and 6.6 Å, respectively (Lin et al. 2012). In pervaporation application, the separation process is also taking advantage of small kinetic diameter of water. However, this process requires heat to turn the feed into vapor

phase, thus facilitating the separation process (Araki et al. 2011). Silica membrane can demonstrate an exceptional sustainability over a long period for the pervaporation application due to the high melting point of silica materials.

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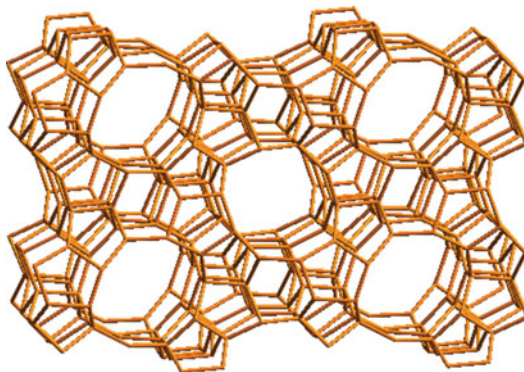
Silicalite Membrane

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Zeolites are a class of crystalline aluminosilicates with highly regular and open microporous structures. More than 200 types of zeolite frameworks have been identified by the Structure Commission of the International Zeolite Association. Zeolite membranes combine the great advantages of inorganic membranes, such as temperature stability and resistance against solvents, with the molecular sieving effect. Zeolite silicalite (MFI, where the three characters indicate the framework type) with Si/Al ratio of ∞ is well known as a hydrophobic zeolite. Figure 1 shows the framework structure of MFI zeolite (International Zeolite Association Web site 2013). There are two channel systems: a straight channel running to (010) with ten-membered ring openings of 5.3×5.6 Å and a sinusoidal channel parallel to the (100) with ten-membered ring openings of 5.1×5.5 Å.

Silicalite membrane was prepared as a self-standing polycrystalline film at first and was very fragile (Sano et al. 1991). Therefore, the silicalite membranes are crystallized on porous supports such as sintered stainless steel disc or



Silicalite Membrane, Fig. 1 Framework structure of silicalite (MFI) zeolite (IZA web. 2013)

alumina disc(tube) with an average pore diameter of $0.5 \sim 2 \mu\text{m}$. Colloidal silica is added to a stirred mixture of tetrapropylammonium bromide (TPABr) and sodium hydroxide in solution, to give a hydrogel with a composition of $0.1 \text{ TPABr} \cdot 0.05 \text{ Na}_2\text{O} \cdot \text{SiO}_2 \cdot 80\text{H}_2\text{O}$. The hydrogel is

transferred to a stainless steel autoclave and kept at 170°C for 48 h. The separation performances can be evaluated by pervaporation measurements using various aqueous alcohol solutions as a feed. Flux and separation factor $\alpha(\text{ROH}/\text{H}_2\text{O})$ are calculated from following equations:

$$\text{Flux (kg/m}^2\text{h)} = \frac{(\text{Weight of permeate, kg})}{(\text{Membrane area, m}^2) \times (\text{Permeation time, h})} \quad (1)$$

$$\text{Separation factor } \alpha(\text{ROH}/\text{H}_2\text{O}) = \frac{[\text{C}_{\text{ROH}}/\text{C}_{\text{H}_2\text{O}}]_{\text{Permeate}}}{[\text{C}_{\text{ROH}}/\text{C}_{\text{H}_2\text{O}}]_{\text{Feed}}} \quad (2)$$

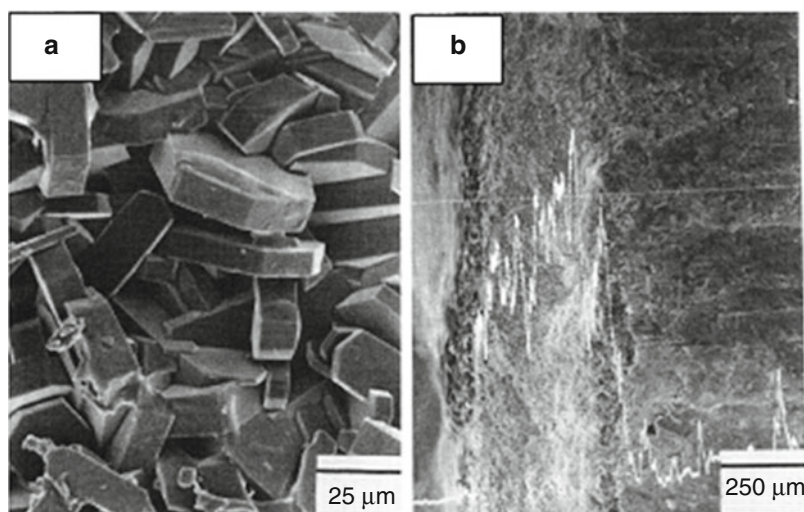
where the C_{ROH} and $\text{C}_{\text{H}_2\text{O}}$ are the volume fractions of alcohols and water, respectively.

Figure 2 shows scanning electron micrographs (SEM) of the outer surface and cross-section of the membrane on the stainless steel support (Sano et al. 1994). The surface is formed of an aggregate of crystals of $10 \sim 30 \mu\text{m}$ and the growth on the support led to a randomly grown crystalline layer. The average thickness of the silicalite layer was confirmed by Si line analysis using energy-dispersive X-ray analysis (EDX). The organic amine used in the silicalite synthesis as a template remains in the channels of silicalite crystals. In order to use the membrane as the separation membrane, the amine must be removed from the

channels by certain procedures. As the silicalite membrane experiences the irregular stresses that arise from a difference in the thermal expansion between the support and the silicalite crystals or from removal of volatile materials from the zeolite framework, cracks are easily formed within the membrane during the treatment process. Therefore, pretreatment conditions of membranes affect strongly the separation performance. As listed in Table 1 (Sano et al. 1994), the silicalite membrane after air-drying at 100°C (containing TPA^+) shows a very low flux combined with a low separation factor below 1, indicating that there is no cracks and pores between silicalite grains within the membrane before the pretreatment. However,

Silicalite Membrane,

Fig. 2 SEM images of (a) outer surface and (b) cross-section of silicalite membrane on stainless steel support (Reproduced from Sano et al. (1994) with the permission of Elsevier)

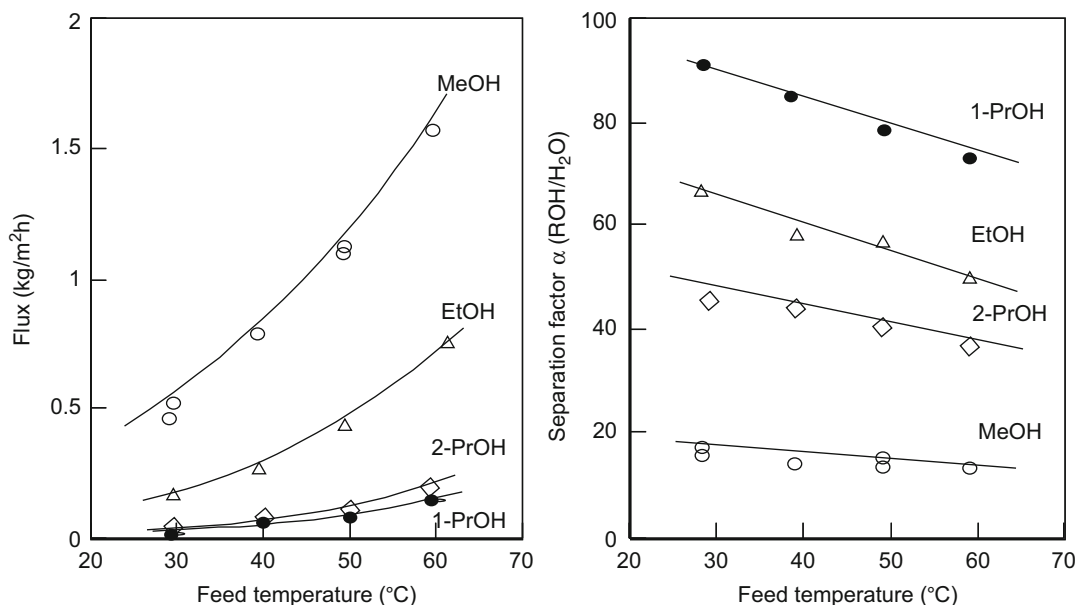


Silicalite Membrane, Table 1 Influence of pretreatment conditions on pervaporation performance of silicate membrane (Reproduced from Sano et al. (1994) with the permission of Elsevier)

Treatment condition			Flux (kg/m ² h)	Separation factor α (EtOH/H ₂ O)
Air-drying	100 °C	12 h	0.00303	0.38
In vacuum	300 °C	6 h	0.00840	0.58
In vacuum	380 °C	6 h	0.0394	7.8
Calcination	500 °C	20 h	0.760	58

Feed temperature: 60 °C

Feed ethanol concentration: 5 vol.%



Silicalite Membrane, Fig. 3 Pervaporation flux and separation factor α for various alcohol/water mixtures (Reproduced from Sano et al. (1994) with the permission of Elsevier). Feed alcohol concentration: 1 mol%

in the case of the membrane after the thermal treatment, the flux and the separation factor increase with an increase in the treatment temperature and period. The membrane calcined at 500 °C to remove the template completely shows the high flux combined with the higher separation factor. The membrane changes from the water-selective membrane to the ethanol-selective one by decreasing the amount of TPA⁺ occluded in the zeolite framework, and the separation of ethanol/water takes place by transport through the zeolite channels. Figure 3 displays effects of the feed temperature on the separation factor and the flux for various alcohol/water mixtures (Sano et al. 1994). The high separation factor

is obtained for 1-propanol/water mixture, although the flux is very low. On the other hand, the higher flux and the lower separation factor are obtained for methanol/water mixture. This can be explained by the differences in the molecular size and the interaction between alcohol and silicalite, methanol being the smallest and the most polar molecule in the group of alcohols tested here.

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Silt Fouling Index (SFI)

► Fouling Index

Silver Recovery by Bulk Liquid Membrane (BLM)

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The occurrence of silver in the natural water environment is of great relevance owing to its toxicity to aquatic plants and animals even at very low concentration, particularly when it is in the free ion form (Ag^+). Silver content into the aquatic environment has increased in the last years owing to its increasing use in the medical and photographic-imaging industry and in the manufacturing of electronics, silverware, and jewelry. An estimated amount of 150 tons of silver is released into the aquatic environment every year. As a result, separation and recovery of silver from industrial wastewaters is of great importance (Altin et al. 2010).

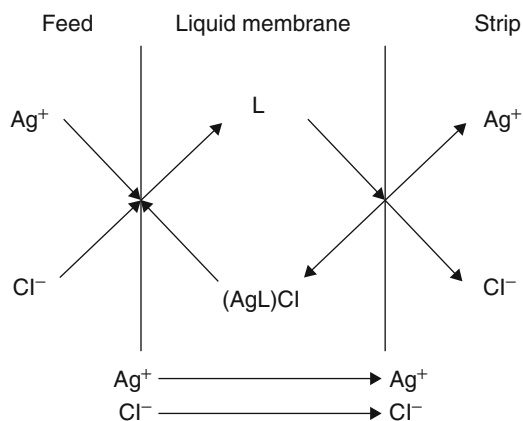
Conventional separation process includes processes like solvent extraction, chemical precipitation, adsorption, and membrane filtration. These techniques efficiently remove metal ions producing water within international health standards, but present some limitations: (i) large amount of solvent required when dilute solutions were processed, making solvent extraction not very cheap and safe, since the used solvents are often chlorinated and sometimes carcinogenic; (ii) production of a large amount of toxic chemical

sludge in which disposal/treatment is a very costly affair and it is not eco-friendly; (iii) poor process selectivity, thus metal recovery is not achieved; (iv) adsorption-based processes are not continuous, requiring regeneration steps that negatively affect process economy.

Carrier-mediated transport through liquid membrane (LM) has been recently considered as one of the most powerful technology to concentrate, separate, and recover metal ions from diluted solutions. LM-based separation techniques combine extraction and stripping into a one-step process, thus having great potential for reducing the solvent inventory requirement and also allowing the use of expensive and highly selective extractant (Molinari and Argurio 2009). The lower capital and operating costs, the low energy consumed, and the high selectivity are the main advantages of LM systems. Thanks to these characteristics, LM-based techniques permit to obtain the recovery of heavy metal ions and the production of water with good quality, resulting into both environmental and economic benefits.

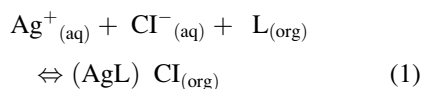
LM-based process includes bulk liquid membrane (BLM), emulsion liquid membrane (ELM), and supported liquid membrane (SLM). BLM usually consists of two aqueous phase (feed and strip) separated by a water-immiscible liquid membrane phase (Molinari and Argurio 2011). Usually the organic solvents, employed as LM phase, are pre-saturated with water by shaking a two-phase mixture and then removing the aqueous phase.

N,N-diethyl-N'-camphanyl thiourea is a very efficient carrier that showed very selective Ag (I) extraction and transport in the presence of Co (II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) using the pH gradient method (Berhe et al. 2006). The aqueous feed phase pH, higher than that one of the strip phase, is usually lower than 5 to avoid metal hydroxides precipitation. The strip phase usually consists of an acid (e.g., HNO_3) dissolved in deionized water. The main operating parameters affecting transport selectivity are the operating pH and the carrier/metal ratio. It was found that process selectivity decreases by increasing the carrier concentration in the LM phase.



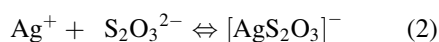
Silver Recovery by Bulk Liquid Membrane (BLM), Fig. 1 Facilitated coupled cotransport for Ag(I) transfer across a liquid membrane

Macrocyclic ligands (e.g., crown) represent a promising class of complexing agents tested in the previous years in silver recovery by BLM (Rounaghi et al. 2008, 2011). In this case the Ag (I) is transported from the feed aqueous phase to the strip phase by the so-called facilitated coupled cotransport (Fig. 1). At feed-LM interface (Fig. 1), the carrier L extracts both Ag^+ ion and the counterion Cl^- by the reversible reaction (1):



The so formed complex diffuses through the membrane towards the stripping solution where the de-complexation reaction takes place, and Cl^- and Ag^+ ions are released. The so regenerated carrier molecule diffuses back to the feed, and the transport cycle begins again (Fig. 1).

Thiosulfate (Rounaghi et al. 2008), cyanide, or sulfite ions or other ligands can be used as stripping agent to improve the permeating flux. Ag^+ ions released in the strip phase react with the ligand to form a complex:



This reaction facilitates the release of Ag^+ ions from the LM phase into the strip phase that

usually is the rate determining step of the membrane transport. The permeating flux largely depends on the nature and concentration of the stripping ligand: for Ag^+ , recovery by BLM with dibenzopyridino-18-crown-6 and the presence of thiosulfate as stripping reagent in the strip phase caused an evident enhancement in transport efficiency.

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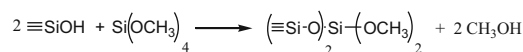
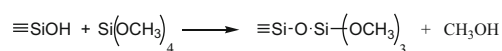
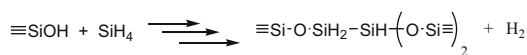
Silylation

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In the 1970s, changing of the pore size of the zeolite silylation with SiH_4 was carried out (Barrer et al. 1977). In general, silylation technique permits the formation of a chemical bond between a chemical species containing silicon (e.g., SiH_4 and $\text{Si}(\text{OR})_4$) and both organic and

inorganic materials. The mechanism of these reactions is showed below.



Silylation is largely used to modify microporous, mesoporous, and nonporous inorganic particles (as zeolites, mesoporous, and nonporous silica materials). Besides, it was also used to cure the defects of both inorganic and mixed-matrix membranes. Some examples are reported below. Zheng and coworkers modified HZSM-5 crystals by silylation with tetraethoxysilane (Zheng et al. 2006). The modified crystals were used in xylene isomerization. Experimental results showed as silylation has significantly different effects on m-Xylene and o- and p-Xylene isomerization because of the inner pores that were hardly influenced. Recently, it was demonstrated the possibility to modify the surface of calcined MCM-41 by means of silylation (Patel et al. 2011). Nitrogen adsorption data and FTIR spectroscopy showed as the trimethylchlorosilane was chemically bonded to the surface of the inorganic material and not just physically adsorbed. Silylated MCM-41 preferentially adsorbed from benzene–water mixtures with a complete rejection of the water. MFI and SAPO-34 membranes were silylated with methyldiethoxysilane to improve their permeation properties (Hong et al. 2005). The results showed that as the chemical modification reduced the B-ZSM-5 pore size as a consequence, an increase of the hydrogen selectivity was detected. However, the hydrogen permeance decreased more than one order of magnitude. For example, H_2/CO_2 separation selectivity increased from 1.4 to 37 at 200 °C. For the SAPO-34 membranes, the results were different. In fact, the selectivity increased but the H_2 permeance remained the same. It is possible to explain these data considering that the methyldiethoxysilane did not enter into the

SAPO-34 pores. Recently, Hong and coworkers found, for ZSM-5 membrane, that the hydrogen selectivity increases while its permeance decreased (Hong et al. 2013). Mixed-matrix membranes (MMMs) are systems designed to improve the properties of a host polymeric matrix taking advantage of peculiar properties of the inorganic fillers (as zeolites). However, using glassy polymer, defects are present at the interface between the particle and polymer. Silylation process is used to modify the zeolite surface in order to compatibilise the inorganic filler with the host matrix (Vrancken et al. 1995). As an example, Clarizia and coworkers (2008) prepared MMMs by using unmodified and silylated (γ -aminopropyldiethoxymethylsilane) zeolite. Better permselectivity values were obtained with the MMMs prepared with modified crystals.

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Simple Emulsion

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An emulsion is a two-phase system consisting of two immiscible liquids, one of which is in the shape of droplets dispersed in the second one. The liquid with droplet shape is referred to as *dispersed phase* or *inner phase*, while the liquid in which these droplets are suspended is called the *continuous phase* or the *external phase* (Morrison and Ross 2002).

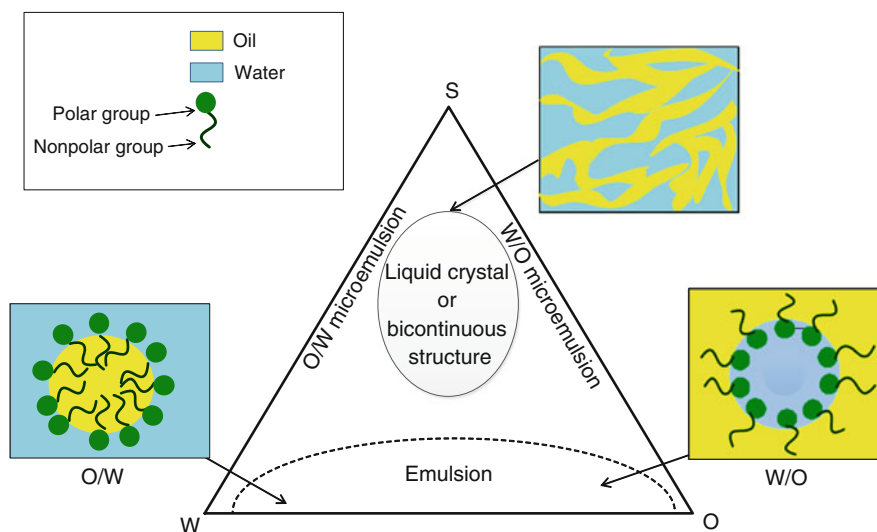
In most cases, emulsions are inherently unstable because they have large interfacial/surface area and high interfacial/surface energy. Consequently, emulsions do not tend to form spontaneously, and energy must be supplied to the bulk phases to induce emulsification (Holmberg et al. 2002). Industrial emulsification processes mainly involve the use of high-pressure

homogenizers, rotor-stator devices, colloid mills, ultrasonic devices, and microfluidizers. Membrane emulsification is another technique used to prepare emulsions. This approach permits one to control the size of the droplets present in the emulsion (Joscelyne and Trägårdh 2000).

Several types of emulsions have been described (Tadros 1983). The most common consists of oil droplets (hydrophobic liquid) dispersed in an aqueous phase (hydrophilic liquid). These systems are referred to as oil-in-water (O/W) emulsions, whereas water droplets suspended in an organic phase are known as water-in-oil (W/O) emulsions.

The structure of an emulsion depends to a great extent on the volume fractions of water, oil, and a third component called *stabilizer*. There are several stabilizing agents, such as surfactants, proteins, polymers, or particles (Binks 2002), with surfactants being the most commonly used stabilizers. The type of emulsion (O/W or W/O) depends on surfactant properties, which should be soluble in the continuous phase (Bancroft 1913, 1915).

This empirical observation can be rationalized by considering the interfacial tension at the



Simple Emulsion, Fig. 1 Ternary phase diagram of an emulsion: *O* oil, *W* water, *S* surfactant

oil-surfactant and water-surfactant interfaces. W/O emulsions result when the volume fraction of water is low. By contrast O/W emulsions are formed when a small volume of oil is dispersed in a large amount of water. Moreover, for systems formulated with similar volume fractions of oil and water, a bicontinuous structure (liquid crystal) is likely to exist. A general ternary phase diagram of an emulsion is shown in Fig. 1.

Emulsions play an important role in the formulation of foods, pharmaceuticals, and cosmetic products because they offer a wide variety of applications as drug delivery carriers or encapsulation systems of bioactive compounds; however, emulsions are also used as metalworking fluids because they combine lubricating and cooling properties (Becher 1983).

Microemulsions are a special type of emulsion characterized by droplet sizes below 100 nm. Its appearance is translucent because light can traverse the emulsion without being scattered (Fanun 2008).

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Sintering Method for Ceramic Membrane Preparation

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Sintering method for ceramic membrane preparation. During ceramic membrane preparation, various shaping techniques such as slip/tape casting, extrusion, and pressing are used to make membrane precursors from particle suspension, slurry, or paste. No matter which process is adopted to prepare the ceramic membrane precursors, sintering (firing step) is necessary to yield the membranes promising mechanical strength and pore structure. When sintering process is conducted at high temperature, contact surfaces of the microparticles are partly sintered together. The final membrane pore structures, such as pore size, porosity, and tortuosity, are directly affected by the sintering parameters including temperature, pressure, particle size, and so on. Generally for the unsupported sintering, with the increase in sintering temperature, membrane pore size distribution becomes narrow, the mean pore size, maximum pore size, and porosity decrease. Moreover, a repeated sintering procedure can further fabricate multilayer membranes after coating step, such as dip-coating, sol–gel processes, and so on (Li 2007).

The price of ceramic membranes is high, so it is worthy to find the way to reduce its cost, which is very sensitive to sintering temperature, especially when they are used in water treatment (Cui et al. 2011). The cost sintering temperature for high purity alumina ranges between 1500 °C and 1700 °C. There are two general approaches to enhancing sintering kinetics or lowering the sintering temperature for ceramics. The first way is improving powder processing by using fine starting powders and eliminating agglomerates

such as by colloidal routes. The second approach is using sintering aids or additives (Xue and Chen 1991).

During the ceramic membrane preparations, constrained sintering, which involves the use of nonsintering layers, either porous or dense, to constrain the shrinkage in the layer plane, is worth to study. A model (Qiu et al. 2009) has been developed based on the sintering mechanism to calculate the change in the pore size and porosity of a ceramic membrane during sintering process. It was found that the porosity of the supported membrane is greater than the unsupported membrane at the same sintering temperature, thanks to the effect of the rigid substrate. As the sintering temperature increases, the mean pore size decreases for the unsupported membranes but increases for the supported membranes.

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Smart Membranes

► Magnetically Responsive Membranes

Soaps

► Amphiphilic Molecules

Sol–Gel Method for Ceramic Membrane Preparation

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The sol–gel technique is commonly used to obtain the desired pore sizes in the top layer of ceramic membranes. Two main routes, colloidal route and polymer route, have been developed to prepare the sol–gel membranes. In the colloidal route, a metal salt is mixed with water to form a sol, which is coated on a membrane support, where it forms a colloidal gel; in the polymer route, metal–organic precursors are mixed with organic solvent to form a sol, which is then coated on a membrane support, where it forms a polymer gel (Li 2007). Polymeric sols have the potential to fabricate smaller pore sizes than particulate sols as the obtained gel layer is built up of a polymeric network (Lindqvist and Lidén 1997).

After drying the coated sol, gelation takes place. Then, the gel particles become sintered and the membranes are produced after thermal treatment. The sol–gel technique has an advantage that the membrane pore size can be controlled desirably, especially for small pores. So it is commonly used to prepare the desired pore sizes in the top layer. The pore size depends on the particle size in the sol. Very small particulate sols are required to obtain pores in the nanometer range (Leenaars et al. 1984).

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Solid Electrolyte

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Solid electrolytes (SE) also termed “superionic solids” or “fast ion conductors” are solid state ionic materials exhibiting an exceptionally high ionic conductivity, in the range of ionic conductivities of liquid/aqueous electrolytes (Agrawal and Pandey 2008). They found applications in different electrochemical systems, like batteries and fuel cells, since their use eliminates leakage problems associated with liquid electrolytes and improves system safety and durability. In electrochemical systems, (see “► [Electrochemical Processing](#)”) in addition to charge transport, solid electrolytes serve as separators, i.e., membranes as well.

In general, there are two classes of these materials: inorganic ceramics and organic polymers. In the case of ceramic solid electrolytes, the ionic conduction relies on movement of ionic point defects, which usually implies high ionic conductivity only at elevated temperatures. Examples of these materials utilizing O_2^- ion as a charge carrier are yttria stabilized zirconia (YSZ), scandia stabilized zirconia (ScSZ), as well as perovskite materials such as Sr/Mg-doped lanthan gallate (LSGM) (Sunmdacher et al. 2005). These materials have found an application in high temperature fuel cells and electrolyzers. In addition to oxygen ion conductors, proton conductors and Li-ion conductors are interesting for technical applications. The Li^+ ion conductors have importance for development of Li-ion batteries. Among these materials, $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) showed so far the best conductivity (Fergus).

Solid polymer electrolytes are an ion conducting membranes with ionic conductivity

above $10^{-7} \text{ S cm}^{-1}$ at room temperature (Agrawal and Pandey 2008). For technical applications conductivities higher than $10^{-4} \text{ S cm}^{-1}$ at room temperature, in addition to chemical and thermal stability, the capacity to be manufactured in thin-sheets and low permeability for reactants/products are favored. Solid polymer electrolytes can be roughly classified into three groups: dry solid polymer electrolytes, polymer gel electrolytes, and polyelectrolytes. In the first group, polymer itself serves as a solvent, solvating ionic salts into a polymer host. An example is poly(ethylene)oxide which is effective in solvating lithium salts for application in Li-ion batteries. In the second group, organic or inorganic liquid electrolyte is incorporated into the polymer matrix forming a polymer gel electrolyte. Example is poly(benzimidazole) doped with phosphoric acid, which found an application in high temperature fuel cells and poly(methyl methacrylate) (PMMA) and poly-acrylonitrile (PAN) cross-linked with lithium or sodium salts with applications in batteries. Third group makes so-called polyelectrolytes. They are macromolecules which upon placing into water or other ionizing solvent dissociate into highly charged polymeric molecules. An example is sulfonated tetrafluoroethylene based fluoropolymer-copolymer commercially (Nafion[®]) by DuPont which found an application in low temperature fuel cells and electrolyzers.

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Solid Electrolyte Membrane Reactor

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Solid electrolyte membrane reactor is a type of an electrochemical reactor which utilizes a solid electrolyte (an ion-conducting membrane) as an ion-conducting medium and a separator (Sundmacher et al. 2005). These reactors found an application in electrochemical processing. Examples are fuel cells, batteries, and electrolyzers. Electrochemical oxidation and reduction reactions in **solid electrolyte membrane reactor** take place in porous electrodes which are usually directly applied on different sides of the solid electrolyte. These electrodes are complex composite structures which have to fulfill different requirements. They should possess catalytic activity such that electrochemical reactions can take place; they should be able to conduct electrons and ions which are released or consumed in electrochemical reactions, and they should transport non-charged reactants or products of reactions to or away from the reaction site. In practice it is difficult to satisfy all these requirements. Currently so-called gas diffusion electrodes which found major application in fuel cells and electrolyzers show practically the best balance of mentioned requirements. Gas diffusion electrodes are usually prepared by mixing of a solid electrolyte, with an inert electron-conducting phase (e.g., carbon nanomaterials for low-temperature applications) and catalyst particles (e.g., platinum).

In fuel cells the main goal of operation is conversion of chemical energy of a fuel, typically hydrogen or hydrocarbons into electrical energy with high efficiency. Fuel cells work in a wide temperature range (25–1000 °C), for which different solid electrolytes (ceramics or polymers, see solid electrolytes) are used. Typical examples are solid oxide fuel cells which utilize ceramic oxygen ion-conducting membrane (e.g., yttria-stabilized zirconia) and polymer electrolyte fuel cell where polymer proton-conducting membrane (e.g., sulfonated

tetrafluoroethylene-based fluoropolymer-copolymer, commercially Nafion[®] by DuPont) is used.

Similar to fuel cells, in batteries the main goal of operation is efficient conversion of stored chemical energy into electrical energy. One example is lithium-ion polymer battery. This type of battery exhibits up to date the highest energy density of all batteries (380 Wh kg⁻¹) and allows a great variety of geometries as well as thicknesses of about 1 mm, which has found wide commercial application in cell phones and laptop computers.

Unlike electrochemical energy-conversion devices (fuel cells and batteries), the main purpose of electrolyzers is high production rate of a specific product at high selectivity and low energy consumption. In some cases the desired product and electrical power can be cogenerated. A detailed survey of applications of high-temperature solid electrolyte membrane reactors for production of different industrially relevant products is presented in Garagounis et al. 2011. Although in some cases notable advantages of solid electrolyte membrane reactors in comparison to conventional catalytic reactor have been identified, this technology still did not reach commercial stage.

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Solid Lipid Particles

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Solid lipid particles represent an alternative carrier system to traditional colloidal carriers, such as emulsions, liposomes, and polymeric micro- and

Solid Lipid Particles, Table 1 Methods of preparation of solid lipid particles

Method	Description	Advantages/disadvantages
Emulsification + cooling		
Hot	The lipid is melted at approximately 5–10 °C above its melting point and dispersed under stirring in a hot aqueous surfactant solution of identical temperature. The produced hot O/W emulsion is cooled down to room temperature; the lipid recrystallizes and leads to solid lipid particles	Temperature-induced drug degradation, drug distribution into the aqueous phase during homogenization, complexity of the crystallization step of the nanoemulsion leading to several modifications and/or supercooled melts
Cold	The melt lipid is cooled and the solid lipid ground to lipid microparticles that are dispersed in a cold surfactant solution yielding a pre-suspension. Then this pre-suspension is homogenized at or below room temperature to break in smaller solid lipid particles, the lipid microparticles. The difference between the melting point of the lipid and the homogenization temperature needs to be large enough to avoid melting of the lipid in the homogenizer	Avoid or minimize the melting of the lipid minimizing loss of hydrophilic drugs to the water phase
Emulsification + solvent evaporation	The lipid is dissolved in an organic solvent and the solution is emulsified in an aqueous phase. After evaporation of the organic solvent, the lipid will be precipitated forming solid particles	The use of pollutant organic solvents

nanoparticles. A solid lipid is used instead of a liquid oil as dispersed phase. The term lipid includes triglycerides (e.g., tristearin), diglycerides (e.g., glycerol behenate), monoglycerides (e.g., glycerol monostearate), fatty acids (e.g., stearic acid), steroids (e.g., cholesterol), and waxes (e.g., cetyl palmitate).

The most used methods of preparation of solid lipid particles are listed in Table 1. The emulsification step can be carried out using the conventional mechanical methods or by membrane emulsifications. The selection of the most suitable method depends on the properties of the lipid and the drug incorporated.

Advantages of solid lipid particles include the composition (physiological compounds), the rapid and effective production process including the possibility of large-scale production, and the possibility to produce carriers with higher encapsulation efficiency. Disadvantages include low drug-loading capacities, the complexity of the physical state of the lipid (transformation between different modifications), and the possibility of supercooled melts which cause stability

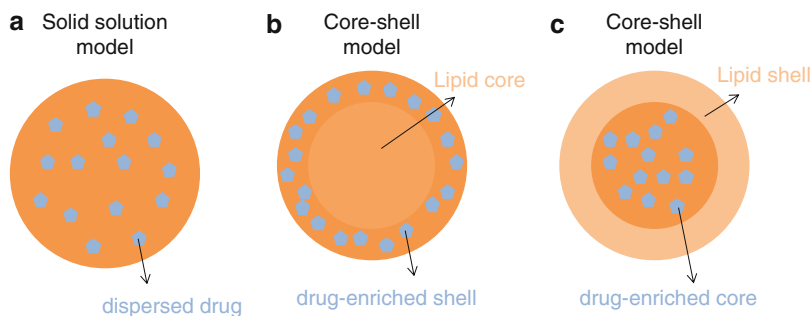
problems during storage or administration (gelation, particle size increase, drug expulsion). Solid lipid particles are one of the novel potential colloidal carrier systems as alternative materials to polymers. They have many advantages such as good biocompatibility and low toxicity, and lipophilic drugs are better delivered by solid lipid particles, and the system is physically stable. Other advantages of solid lipid particles include: control and/or target drug release, improved stability of pharmaceuticals, high and enhanced drug content, better control over release kinetics of encapsulated compounds, enhanced bioavailability of entrapped bioactive compounds, chemical protection of labile incorporated compounds, much easier to manufacture than biopolymeric nanoparticles, and very high long-term stability.

Three drug incorporation models can be considered:

1. Solid solution model. The solid lipid particles matrix is a solid solution (containing the drug dispersed in the lipid matrix) when the particles

Solid Lipid Particles,

Fig. 1 Three drug incorporation models (solid solution model, core-shell models with drug-enriched shell, and drug-enriched core)



are by cold emulsification + cooling and using no surfactant or no drug-solubilizing surfactant (Fig. 1a).

2. Core-shell model, drug-enriched shell. A drug-enriched shell is obtained when the drug precipitates first before the lipid recrystallizes. This should be obtained when dissolving a drug in the lipid melt at or close to its saturation solubility. Cooling of the emulsion leads to a supersaturation of drug in the melted lipid and subsequently to drug crystallization prior to lipid crystallization (Fig. 1b).
3. Core-shell model, drug-enriched core. Further cooling will finally lead to the recrystallization of the lipid surrounding the drug core as a membrane. This lipid membrane will contain only drug in such a concentration corresponding to the saturation solubility of the drug at the recrystallization temperature of the lipid. That means it will result in a drug-enriched core surrounded by a lipid shell (Fig. 1c).

Solid lipid particles have been introduced as a novel drug delivery system for pharmaceutical drugs in various application routes (Müller et al. 2000). They also represent a promising carrier system for cosmetic active ingredients due to their numerous advantages over existing conventional formulations (Müller and Dingler 1998). Solid lipid particles have potential multiple applications in the food and agricultural industries (Weiss et al. 2008). They are of particular interest to manufacturers of functional foods that are looking for novel ways to include lipophilic but chemically sensitive bioactive compounds.

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Solubility

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Solubility (*C*) is a thermodynamic quantity characterizing the distribution of chemical species between different phases in equilibrium. In particular, the solubility (of a *solute* in a *solvent*) expresses the amount of chemical species (*solute*), dissolved in a fixed amount of an uptaking species (*solvent*), at equilibrium. The equilibrium is reached at the end of a *sorption* (or *absorption*) process, in which the solute molecules spontaneously move from the original phase to the solvent phase and form a homogenous mixture (solution) of molecules interacting with noncovalent bonds. Often the

term “solubility” is also used to indicate the sorption process.

The solubility value is measured when the solute net mass transfer is zero and an equal chemical potential of the solute species in the two phases is attained. The time required to reach such equilibrium state depends on the diffusivity of the solute in the solvent in the state of the solution, on the geometry of the system, and the boundary and initial conditions of the mass transfer problem. The solubility of a solute in a solvent depends on the respective chemical nature and thermodynamic state but also on binary interactions and can be obtained by solving the phase equilibrium problem, with an appropriate model that allows to represent the chemical potential.

The solubility is thus a measure of solute concentration at equilibrium and can be expressed in mass, molar, or volume terms and using different units as reported in Table 1.

In membrane processes governed by the solution-diffusion framework like gas and vapor separation, pervaporation, and liquid/liquid separation, the membrane is the solvent in equilibrium with the feed and permeate fluid phases on the upstream and downstream side, respectively. The concentration of solute i absorbed onto the membrane boundaries is equal to $C_{i,\text{up}}$ and $C_{i,\text{down}}$, respectively. The difference $\Delta C_i = C_{i,\text{up}} - C_{i,\text{down}}$ ensures solute mass flux across the membrane, according to Fick's law.

Solubility can be measured via gravimetric, manometric, optical methods, etc. (Czichos

et al. 2006) and is usually expressed through curves (solubility isotherms) reporting isothermal data.

According to the phase rule, in the system formed by two phases (the original solute phase and the solvent phase), one solvent and N_S solute species, the number of variables required to univocally define the state of the system is N_S+1 .

The solubility isotherm of a solute i in a solvent reports the solubility of that solute in the solvent versus the composition of the solute in the original solute phase, which can be expressed with different quantities depending on the state of aggregation of such phase. Some examples are given below.

For a *gaseous* solute phase, the *fugacity* f_i or the *partial pressure* p_i , if the gas phase is ideal, is used.

For a *vapor* solute phase, the activity (a_i) is preferentially used, i.e., the ratio between the *fugacity* in the current state and the fugacity in a reference state, that is usually chosen to be the vapor/liquid saturation point of the pure solute at the same temperature:

$$a_i = \frac{f_i(T, p, y_i)}{f_i^0(T, p_{i,\text{SAT}}(T))} \xrightarrow[\text{pressure}]{\text{low}} \frac{py_i}{p_{i,\text{SAT}}(T)} \quad (1)$$

For *pure liquid solute phases*, the solubility, as many other liquid-state properties, is to all practical purposes a weak function of pressure, and its value can be assumed unique at a fixed temperature.

For *multicomponent liquid solute phases*, the activity a_i can be used, being γ_i the activity coefficient:

$$a_i = x_i \gamma_i^{\text{ideal}} \equiv x_i^{\text{mixture}} \quad (2)$$

Solubility, Table 1 Units used for solubility C of fluids in membranes. 1 solute, 2 solvent

g_1/g_2
g_1/cm_2^3 ^a
$\text{mol}_1/\text{mol}_2$
mol_1/g_2
$\text{mol}_1/\text{cm}_2^3$ ^a
$\text{cm}_1^3(STP)/\text{cm}_2^3$

STP standard temperature and pressure, 1 atm and 25 °C, 1 $\text{cm}^3(STP) = 4.461 \cdot 10^{-5}$ mol

^aUsually cm^3 of pure solvent

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Solubility and Partitioning

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When a solute is added to two immiscible (or partially miscible) phases, it will distribute unevenly between them, giving rise to the so-called solute partitioning between the phases. The distribution of a solute among coexisting phases, in particular liquid phases, is a phenomenon of industrial importance in several purification processes such as liquid extraction, partition chromatography, etc.

In membrane processes the partitioning occurs between the fluid phase (feed, permeate) and the membrane phase.

Partitioning of the solute i between the solute (I) and membrane (II) phase can be defined with the partition or distribution coefficient $K_{i,I/II}$ defined as the ratio between the concentration (solubility) of solute in the membrane phase and the concentration (solubility) of solute in the external phase, that is normally lower than unity:

$$K_{i,I/II} = \frac{C_{i,I}}{C_{i,II}}$$

Partition coefficient of solute i between phase I and phase II.

Solubility Coefficient (S)

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The solubility coefficient, S_i , of a gas i in a membrane is the ratio between its solubility C_i in the

membrane and its fugacity f_i or partial pressure p_i in the gas phase at constant temperature:

$$S_i = \frac{C_i}{f_i} \quad (1)$$

For gas sorption in polymer membranes, a common unit is $\text{cm}^3(\text{STP})/(\text{cm}^3(\text{pol}) \text{ atm})$. The solubility coefficient of a low-pressure gas in a liquid is the reciprocal of Henry's law coefficient H .

In the case of gas sorption in polymer membranes, of particular interest is the *infinite dilution solubility coefficient*, S_0 , that is evaluated in the limit of infinite dilution or zero pressure of penetrant in the gaseous phase.

$$S_{i0} = \lim_{p \rightarrow 0} \frac{C_i}{f_i} = \lim_{p \rightarrow 0} \frac{C_i}{p_i} \quad (2)$$

For vapor solubility in polymer membranes, the activity-based solubility coefficient is sometimes also used, $S_i p_{SAT}$, that is the ratio between solubility and corresponding penetrant activity, if the vapor phase is ideal.

The solubility coefficient at fixed fugacity represents the slope of the straight line connecting a point on the solubility isotherm to the origin (See Fig. 1b); S_0 is the slope of the tangent to the gas solubility isotherm in the zero-pressure limit (see Fig. 1a).

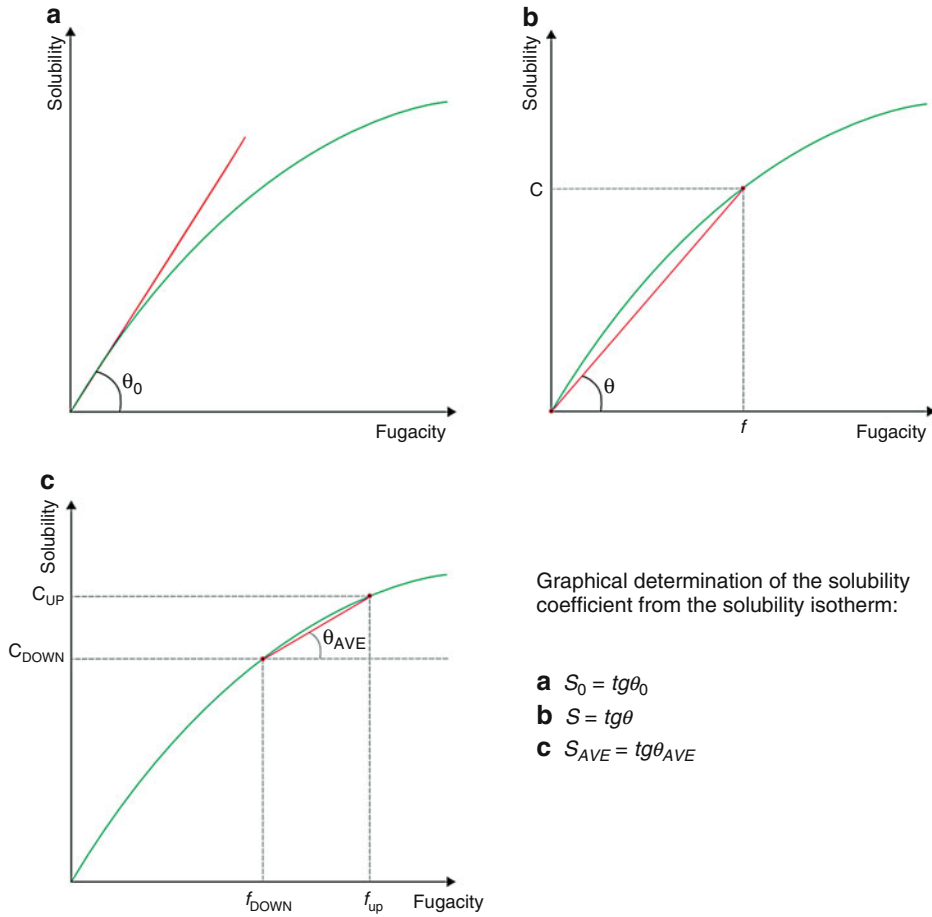
In the solution diffusion transport of solute i through membranes, Fick's law holds true for the gas flux inside the membrane at steady state:

$$J_i = D_i \frac{\Delta C_i}{l} \quad (3)$$

On the other hand, the permeability of gases in membranes is defined with respect to the pressure gradient of penetrant i , in steady state:

$$J_i = P_i \frac{\Delta f_i}{l} \quad (4)$$

Therefore, one has that



Solubility Coefficient (S), Fig. 1 Graphical determination of the solubility coefficient from the solubility isotherm: (a) infinite dilution solubility coefficient, (b) solubility coefficient, (c) average solubility coefficient

$$\begin{aligned}
 D_i \frac{C_{i,up} - C_{i,down}}{l} &= P_i \frac{f_{i,up} - f_{i,down}}{l} \rightarrow P_i \\
 &= D_i \frac{C_{i,up} - C_{i,down}}{f_{i,up} - f_{i,down}} \equiv D_i S_{i,AVE}
 \end{aligned}
 \quad (5)$$

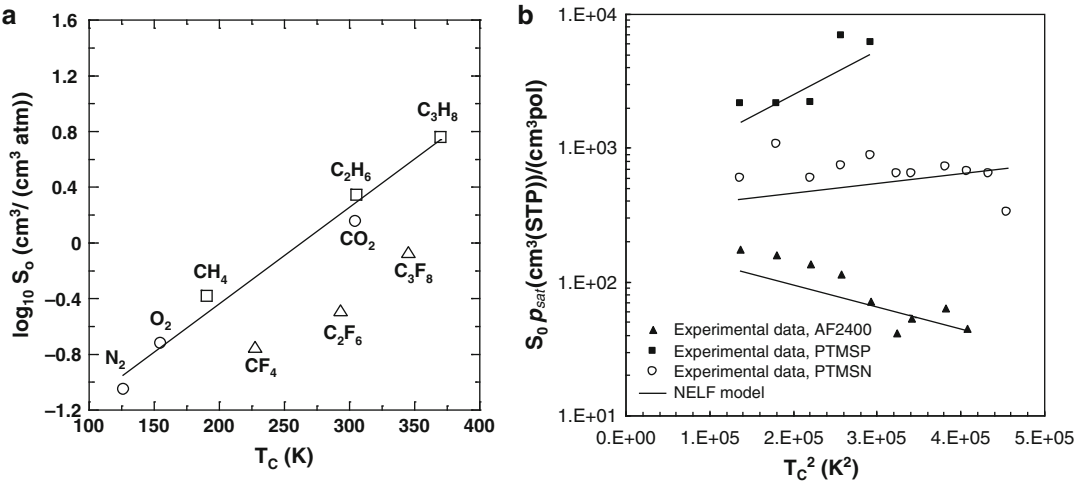
where $S_{i,AVE}$ is the slope of the straight line connecting the upstream and downstream points on the solubility isotherm (see Fig. 1c). In the figure, the case of a concave down solubility isotherm has been taken as an example to represent the graphical meaning of S (here and in the following the pedix i is omitted for simplicity sake).

Correlations for the Solubility Coefficient

The sorption of a gas in a membrane requires condensation of the gas, followed by mixing with the membrane molecules. Therefore, the higher the condensability of the membrane and its compatibility with the membrane material, the larger its solubility in the membrane at fixed temperature. A convenient measure of the penetrant condensability is the critical temperature, and empirical correlations of the following kind have been proposed in the literature for data relative to an homologous set of penetrants in a given polymer at fixed temperature (Bondar et al. 1999; Stern et al. 1969):

Solubility Coefficient (S), Table 1 Experimental and predicted values of correlation coefficients for the solubility coefficient of gases in glassy membranes (De Angelis et al. 2007)

	$\ln(S_0) = a + bT_C, \quad S_0 \text{ in } \text{cm}^3_{\text{gas}}(STP)/(\text{cm}^3_{\text{pol}}\text{atm})$			
	Experimental value		Predicted, NELF model	
35 °C	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
PC	0.0192	−4.0994	0.0226	−5.0123
PSf	0.0209	−4.2394	0.0215	−4.5165
PPO	0.0238	−3.6305	0.0242	−4.0788
PMMA	0.0212	−5.0132	0.0219	−4.8131



Solubility Coefficient (S), Fig. 2 Solubility coefficient of gases in: (a) rubbery PDMS membrane – fluorocarbon penetrants follow a different trend with respect to the other ones due to lower solubility (Adapted from De Angelis

et al. 1999). (b) Activity-based solubility coefficient of vapors in membranes can follow different trends with the vapor critical temperature: increasing, constant, or decreasing (Adapted from Galizia et al. 2012)

$$\ln(S_0) = a + bT_C \text{ at constant temperature} \quad (6)$$

$$\ln(S_0) = a' + b'T_C^2 \text{ at constant temperature} \quad (7)$$

$$\ln(S_0) = M + N(T_C/T)^2 \quad (8)$$

For rubbery polymers, the above correlation can be retrieved using Flory-Huggins theory and a few assumptions (Gee 1947). For glassy polymers, the correlation can be reproduced efficiently by the NELF model (De Angelis et al. 2007), as it can be seen in Table 1.

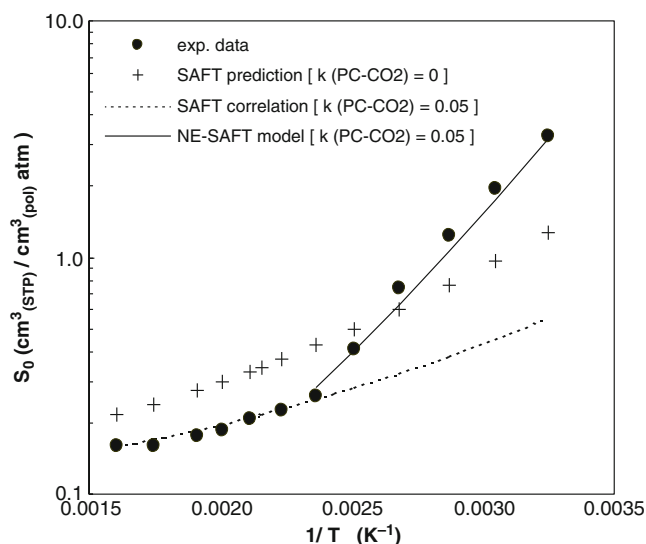
Other authors correlate the values of S_0 to other condensability-related parameters, such as the Lennard-Jones parameter (Van Krevelen 1990), critical volume, surface area (Yampolskii

et al. 2000), etc. It must be noticed that, when different series of penetrants are considered, the solubility data may fall on separate correlating lines. This is the case of fluorocarbon penetrants in PDMS which show lower solubility than the other gases of similar critical temperature, due to lower interaction with the polymer (De Angelis et al. 1999) (Fig. 2a).

The activity-based solubility coefficient of gases can increase or decrease with critical temperature (Galizia et al. 2012) (see Fig. 2b) because, being normalized for the different condensability of penetrants, accounts only for the mixing effects, which can be positive or negative depending on the gas-polymer interactions.

Solubility Coefficient (S),

Fig. 3 Solubility coefficient at infinite dilution of CO₂ in PC as a function of reciprocal temperature. Model results are also reported: SAFT equation-of-state and nonequilibrium SAFT model (Adapted from Giacinti et al. 2005)

**Dependence on Temperature**

The sorption of a gas or vapor into a solid membrane is usually an exothermic process in which the most important thermal effect is the negative heat of condensation of the fluid in the membrane phase. In addition, there is a mixing term which can be positive or negative depending on the solute-membrane couple, but is usually lower, in absolute value, than the condensation term.

Therefore, the solubility coefficient values for gases and vapors in polymer membranes decrease with temperature, usually according to an Arrhenius type of dependence, as follows:

$$S = S(T_0) \exp\left(-\frac{\Delta H_S}{RT}\right) \quad (9)$$

The heat of sorption assumes a different value for the rubbery and glassy state; in particular the higher value is observed in the glassy phase of the same amorphous polymer. This behavior can be seen, for instance, by reporting S_0 values as a function of $1/T$ (Fig. 3): the change of slope occurs at the membrane glass transition temperature.

For liquid solutes, there is no condensation term and the thermal effect associated to sorption in the membrane can be positive or negative.

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Solubility of Gases in Membranes

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The solubility of gases in membranes directly affects the gas separation performance in processes governed by the solution-diffusion mechanism. Gaseous solutes (penetrants) are absorbed onto the upstream membrane side, diffuse through the membrane, and desorb from the membrane in the downstream side toward the permeate gas phase. According to Fick's law, in steady state, the flux of penetrant i through the membrane is associated with the diffusivity and concentration gradient $\Delta C_i/l$ as follows:

$$J_i = D_i \frac{\Delta C_i}{l} \text{ (steady state)} \quad (1)$$

Amorphous Rubbery Membranes

In polymer membranes above their glass transition point (*rubbery*), the solubility has a unique value once the temperature and penetrant fugacities are fixed. The solubility isotherms of gases in rubbers are linear, for light gases, or concave up for non-light gases and vapors (Fig. 1i). High-pressure gases (e.g., supercritical CO₂) are shown to exhibit a decrease of slope of the solubility isotherms at pressures above the critical one; in such range the fluid behavior resembles the liquid one, in which the properties vary slightly with the pressure (Fig. 1ii).

If the rubbery polymer is cross-linked, the swelling of the rubbery matrix and the solubility are lower than those measured in the uncross-linked rubber; indeed cross-linking can prevent

plasticization of the membrane by highly soluble vapors. The solubility of gases in rubbery membranes can be estimated with the Flory-Huggins and related activity coefficient models or with equation of state models (lattice fluid, SAFT, PHSC, etc.) (De Angelis and Sarti 2011).

Amorphous Glassy Membranes

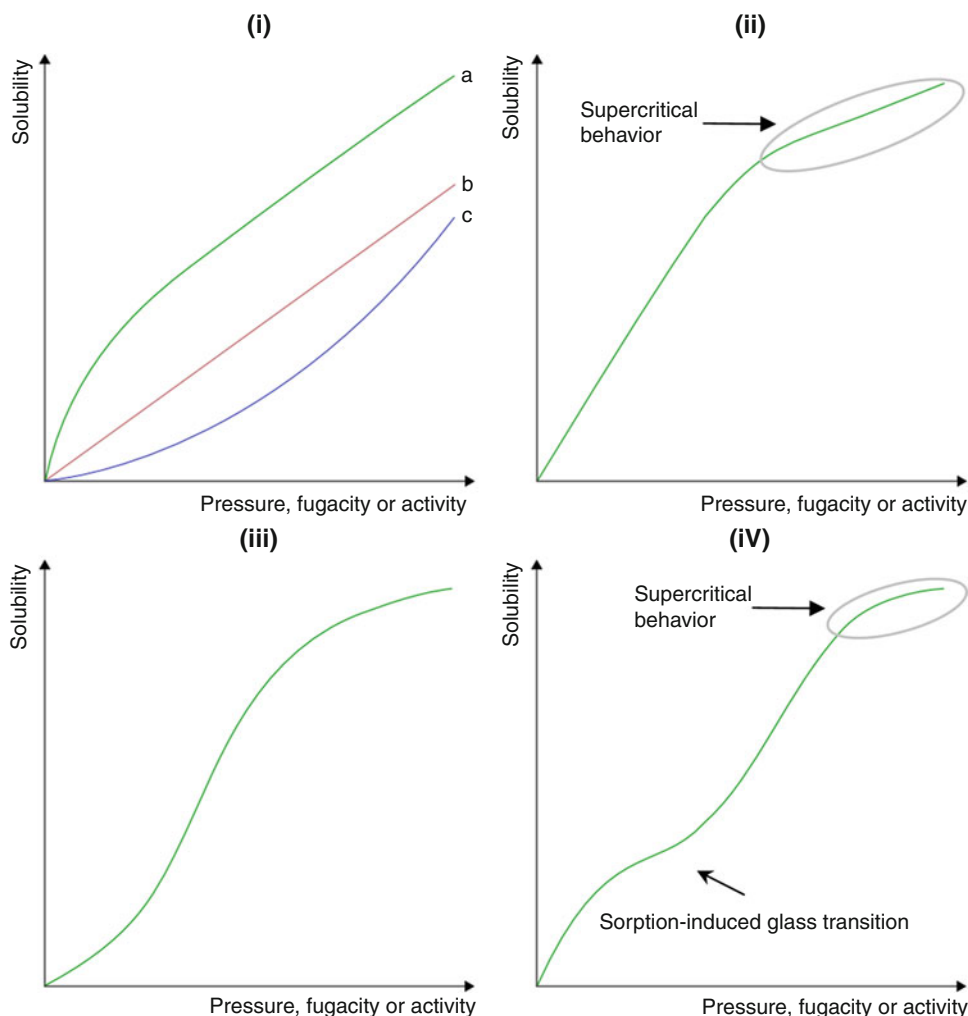
Membranes below their glass transition point (*glassy*) are not at equilibrium due to the hindered mobility of polymeric chains, and the properties, including the solubility, can vary with time, either because of aging or as a consequence of thermal, mechanical, and chemical treatments. The state of the glassy membrane has to be defined with a proper parameter, such as the glassy membrane density, or equivalently the fractional free volume, in addition to the other state variables.

The solubility isotherms of gases in glassy membranes are linear for light gases or concave down for other gases and vapors (Fig. 1i). Some vapors (e.g., alcohols) in certain glassy polymers can show a sigmoidal shape of the solubility isotherm (Fig. 1iii).

If the glassy membrane is close to its glass transition temperature and/or if the penetrant has high solubility in the membrane and is able to significantly swell and plasticize the membrane, a glass transition can be observed at constant temperature by increasing the gas pressure (*sorption-induced glass transition*), which occurs as a change of concavity of the solubility isotherm (Fig. 1iv). The solubility in glassy membranes can be modeled by the dual mode empirical model (Barrer et al. 1958) or the nonequilibrium approaches proposed by Doghieri and coworkers (Doghieri and Sarti 1996, De Angelis and Sarti 2011).

Semicrystalline Membranes

The crystalline phase is considered impermeable and insoluble, and the solubility of the matrix is given by



Solubility of Gases in Membranes, Fig. 1 Different shapes of solubility isotherms in polymeric membranes. (i) (a) Sorption of gases and vapors in glassy membranes, (b) sorption of light gases in glassy and rubbery membranes, and (c) sorption of gases and vapors in rubbery membranes. (ii) Supercritical sorption in rubbery

membranes (e.g., CO₂ in PDMS), (iii) sigmoidal sorption of polar vapors in hydrocarbon glassy membranes (e.g., alcohols in PTMSP) (Nakanishi et al. 1987), and (iv) CO₂ sorption in an initially glassy membrane (e.g., PMMA) (Carlà et al. 2005)

$$C_i = (1 - \phi_{CR})C_{i,AM} \quad (2)$$

where ϕ_{CR} is the fraction of crystalline phase and $C_{i,AM}$ is the solubility in the amorphous phase. In some cases, however, the presence of the crystalline phase may vary the amorphous phase properties with respect to the pure state ones. In particular, it can reduce the specific

volume or reduce the ability of the matrix to swell, with a consequent lower solubility of the amorphous phase with respect to the pure phase: such phenomenon has been modeled invoking an additional pressure term, using both molecular and equation of state methods (Memari et al. 2010, Minelli and Angelis 2014).

Composite (Mixed Matrix) Membranes

In mixed matrix membranes, the solubility C_i of a fluid in a mixed matrix membrane (MMM) can be estimated with an additive rule based on the polymer (P) and filler (F) fractions in the MMM, and the solubility values in the corresponding pure phases, $C_{i,P}$ and $C_{i,F}$:

$$C_i = \phi_P C_{i,P} + (1 - \phi_P) C_{i,F} \quad (3)$$

However, in many cases, a deviation from this rule is observed. The filler phase, if porous, can be obstructed by contact with the polymer and its sorption capacity lowered. The imperfect adhesion between polymer and filler phase can modify the morphology and properties of the polymeric phase and its sorption capacity, as in the case of mixed matrices formed by glassy polymers and nanometric silica. In such systems the solubility increases, due to an increased free volume of the polymer (De Angelis and Sarti 2012).

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Solubility Parameter

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The ► **solubility parameter** δ is a thermodynamic quantity introduced by Hildebrand and Scatchard (HS) to describe the behavior of the so-called regular solutions. Such solutions have a negligible mixing volume and excess entropy of mixing, so that the excess Gibbs free energy coincides with the mixing enthalpy. The HS model uses the idea of cohesive energy density (CED), that is, the difference between the internal energy of the system and that of the corresponding system in the ideal gas state, per volume of liquid substance, estimated as follows: (Sandler 2006)

$$\begin{aligned} CED &= \frac{(\Delta \tilde{U}_{VAP})_{L \rightarrow IG}}{\tilde{V}_L} \\ &= \frac{(\Delta \tilde{H}_{VAP})_{L \rightarrow IG} - RT}{\tilde{V}_L} \end{aligned} \quad (1)$$

And the solubility parameter δ is defined as:

$$\delta \equiv \sqrt{CED} \quad (2)$$

The solubility parameter is related to the molar excess Gibbs free energy, $\tilde{G}^{EX}$, and to the mixing enthalpy, $\Delta \tilde{H}_{MIX}$, by the following expression valid for a binary mixture:

$$\begin{aligned} \tilde{G}^{EX} &= \Phi_1 \Phi_2 (x_1 \tilde{V}_1 + x_2 \tilde{V}_2) (\delta_1 - \delta_2)^2 \\ &= \Delta \tilde{H}_{MIX} \end{aligned} \quad (3)$$

where:

$$\Phi_i = \frac{x_i \tilde{V}_i}{x_1 \tilde{V}_1 + x_2 \tilde{V}_2} \quad (4)$$

And for the activity coefficient of species i :

$$RT \ln \gamma_i = \tilde{V}_i \Phi_j^2 [\delta_i - \delta_j]^2 \quad (5)$$

The model is predictive for the solubility as far as the δ values of the two species are known and the theory can depict correctly the physical behavior of the mixture; indeed the equilibrium composition or solubility can be found applying the phase equilibrium condition for the solute species.

Although the HS theory is not always appropriate, especially for solutions containing polymers, as it does not account for mixing volume and excess entropy of mixing, and it uses the geometric mean rule assumption for the binary interactions between unlike molecules, the δ value is widely used to estimate a priori the mutual solubility of two species. Two species with similar δ values show little excess free energy and are mutually soluble in the entire composition range. Two components with dissimilar solubility parameters have high values of the excess free energy and can show a miscibility gap.

In gas sorption in membrane systems the values of solubility is higher if the gas and polymer solubility parameters are similar, and lower if they are dissimilar, at fixed condensability of the gaseous penetrant.

In some cases, it is evident that the solubility of different fluids in a membrane is strongly correlated to the solubility parameter difference.

Normally δ values are tabulated at 25 °C and their value is almost constant with temperature. For fluids, the values are easily retrievable. For polymers, the vaporization quantities cannot be measured, and the δ values can be estimated from experimental mixing data or with group contribution methods like the ones by Hoftyzer and Van Krevelen and by Hoy (Van Krevelen 1990). In both methods the same assumption is made that the cohesive energy is not only represented by the dispersion interaction forces between molecules, as originally assumed by the HS theory, but it accounts also for the polar groups interactions and for the hydrogen bonds:

$$CED = CED_D + CED_P + CED_H \quad (6)$$

And correspondingly:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (7)$$

Some values of the solubility parameters for polymers of interest in membrane separations, as measured

Solubility Parameter, Table 1 Solubility parameter values for some polymers

Polymer	δ (J ^{1/2} /cm ^{3/2}), experimental from mixing data	δ (J ^{1/2} /cm ^{3/2}), estimated with group contribution methods
Polyethylene	15.8–17.1	16.0
Polypropylene	16.8–18.8	17.0
Polyisobutylene	16–16.6	16.4
Polystyrene	17.4–19	19.1
Poly(vinyl chloride)	19.2–22.1	19.7
Poly(vinylidene chloride)	20.3–25.0	20.6
Poly (tetrafluoroethylene)	12.7	11.7
Poly (chlorotrifluoroethylene)	14.7–16.2	15.7
Poly(vinyl alcohol)	25.8–29.1	–
Poly(vinyl acetate)	19.1–22.6	19.6
Poly(methyl acrylate)	19.9–21.3	19.9
Poly(ethyl acrylate)	18.8–19.2	19.2
Poly(methyl methacrylate)	18.6–26.2	19.0
Polyacrylonitrile	25.6–31.5	25.7

from mixture data and as estimated by the group contribution method of Hoftyzer and Van Krevelen are reported in Table 1 (Van Krevelen 1990).

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Solubility-Selective Membrane

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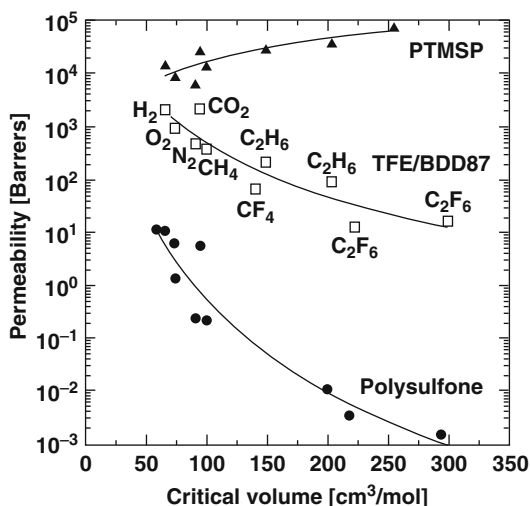
This term usually refers to polymeric membranes used for gas separation process and indicates those membranes whose selectivity is governed

by the solubility, rather than diffusivity, of the penetrants in the membrane. Indeed in gas separation with polymeric membranes, the selectivity α is the product of a solubility-selectivity, α_S , and of a diffusivity-selectivity term, α_D , according to the solution-diffusion model. It is generally thought that smaller penetrants are more permeable than large ones in solids due to the large diffusivity differences between small and large penetrants, but this trend, although very common, is not always valid.

In the solubility-selective membrane, some large, condensable penetrants are more permeable than the small, poorly condensable penetrants, due to their higher solubility and despite their lower diffusivity. This type of membranes is sometimes also called “vapor selective” or “reverse selective” as opposed to the “size-selective” ones, because vapors are usually more permeable than gases. Some rubbery polymers used in gas separation follow this trend, as, for instance, the polydimethylsiloxane (PDMS). In glassy polymers, the solubility-selective behavior is preferentially shown by those polymers characterized by rather large free volume, i.e., higher than around 15 % (polytrimethylsilyl propyne (PTMSP), poly(4-methyl-2-pentyne) (PMP), etc.) In those polymers, the diffusivity is a weakly decreasing function of the penetrant size, and thus the diffusivity-selectivity between small and large penetrants has limited values. On the other hand, the solubility is a strongly increasing function of the penetrant size or condensability; thus, for a couple of penetrants A and B, where A is larger than B, one can have that

$$\begin{aligned} \alpha_{S,A/B} &\gg 1 & \alpha_{D,A/B} &\leq 1 \\ \rightarrow \alpha_{S,A/B} &> (\alpha_{D,A/B})^{-1} & \rightarrow \alpha_{A/B} &= \alpha_{S,A/B} \cdot \alpha_{D,A/B} > 1 \end{aligned}$$

The permeability of different gases versus their size is reported in Fig. 1 for three types of polymer membranes: a solubility-selective one (PTMSP), a slightly diffusivity-selective one (amorphous Teflon® AF2400), and a strongly diffusivity-selective one (polysulfone, PSf). The permeability and selectivity values of some



Solubility-Selective Membrane, Fig. 1 Permeability coefficients at 35 °C as a function of penetrant size in TFE/BDD87 (Teflon AF2400), poly(1-trimethylsilyl-1-propyne) (PTMSP) and polysulfone (Merkel et al. 1999) (Reprinted with permission from Merkel et al. (1999). Copyright 1999 American Chemical Society)

Solubility-Selective Membrane, Table 1 Permeability and selectivity of some solubility-selective polymer membranes

	Permeability/N ₂ permeability		
	PTMSP (Javaid 2005)	PDMS	PMP (25 °C) (Morisato et al. 1996)
CH ₄	2.44	3.15	2.2
C ₃ H ₈	4.81	18.65	3.5
n-C ₄ H ₁₀	12.51		30

solubility-selective membranes are reported in Table 1.

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Solute Reverse Transport

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Solute reverse transport refers to the diffusion of solutes from a high-concentration draw solution (DS) to a low-concentration feed solution (FS) in forward osmosis (FO) and pressure retarded osmosis (PRO). For an ideal semipermeable membrane with 100 % solute rejection, draw solutes are perfectly rejected such that there is no solute reverse transport. Real membranes do not have perfect rejections against solutes. Under a concentration gradient across the FO, the solutes diffuse from DS to FS. Because this draw solute flux is opposite to the direction of water flux, it is named as (draw) solute reverse flux. Solute reverse transport can lead to various negative impacts. In FO and PRO processes, draw solutes diffused to the FS reduce the DS concentration. The replenishment of draw solutes can significantly increase the operational cost. Additionally, draw solutes transported into feed solution side may induce severe internal concentration polarization (ICP) and therefore reduce the FO water flux (Zou et al. 2011). Certain types of draw solutes, once diffused into the FS, may interact with contaminants in the FS (e.g., Ca^{2+} from the DS can interact with foulants in the FS to induce the severe membrane fouling). Therefore, understanding and controlling the solute reverse transport is critical for more efficient FO and PRO operations.

In FO, the reverse solute flux (J_s) and water flux (J_v) can be mathematically expressed with the following equations (Tang et al. 2010):

$$J_s = B\Delta C = B(C_{\text{draw}} - C_{\text{feed}}) \quad (1)$$

$$J_v = A\Delta\pi = A(\pi_{\text{draw}} - \pi_{\text{feed}}) \quad (2)$$

where C_{draw} and C_{feed} are the concentration of draw solution and feed solution, respectively. π_{draw} and π_{feed} are the osmotic pressure of draw solution and feed solution, respectively. A is the water permeability of membrane and B is the solute permeability of membrane. The values of A and B can be determined by reverse osmosis testing. Substituting the Van't Hoff equation into Eqs. 1 and 2, one can get the relationship between J_s and J_v :

$$J_s = \frac{B}{A\beta R_g T} J_v \quad (3)$$

where β is the Van't Hoff coefficient, R_g is the universal gas constant, and T is the absolute temperature. From Eq. 3, we noticed that J_s is strongly influenced by B/A , which is an indicator of the membrane selectivity.

The reverse solute flux in PRO process is given by She et al. (2012)

$$J_s = \frac{B}{A\beta R_g T} J_v \left(1 + \frac{A\Delta P}{J_v} \right) \quad (3)$$

where ΔP is the transmembrane pressure difference.

Because of the high pressure used in PRO and the PRO membrane is generally not well supported by spacers, mechanical stress in the membrane tend to deteriorate the membrane rejection under PRO operation. Thus, the reverse solute flux tends to be much high in PRO compared to that in FO.

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Solution-Diffusion Mechanism

► Principle of Gas Separation

Solvent Evaporation Membrane Crystallization

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Solvent evaporation membrane crystallization is a membrane-assisted crystallization configuration where the substances to be crystallized are dissolved in an undersaturated solution located at the feed side of the membrane. In the current general conception, a nonvolatile solute that is likely to be crystallized (defined as the crystallizing solution or feed or retentate) is contacted, by means of a (macro)porous membrane, with a solution on the distillate side. The membrane might be made by polymeric or inorganic materials or by a combination of both in a hybrid or composite configuration. Hollow fibers as well as flat sheet membranes can be employed indifferently.

When the membrane is prevented to be wet from the adjacent solutions, no mass transfer through its porous structure is observed directly in liquid phase but the two contacted subsystems are subjected to mass inter-exchange in vapor phase. Wetting of the membrane, with the consequent deleterious direct passage of liquids, can be avoided when the pressure of the solutions facing it is lower than the entry limit (P_{entry}), defined by Young-Laplace's equation (Atkins 1998). This means that hydrophobic membranes can be used for hydrophilic (aqueous) crystallizing solutions and hydrophilic membrane materials are suitable for hydrophobic (or oleophilic) solutions.

For a pressure lower than P_{entry} , the two liquids are stopped at the entrance of each pore on both membrane sides, thus generating a curved profile. Crystal nucleation and growth in the feed solution

are induced by generating supersaturation. This can be done either by removing the solvent from the crystallizing solution, thus increasing solute concentration up to the overcoming of its solubility limit. Accordingly, the role of the membrane is not simply as a sieving barrier to select the transport of specific components but instead as a physical support which, by removal of the vaporized solvent or by addition of the antisolvent, generates and sustains a controlled supersaturated environment in which crystals can nucleate and grow.

The driving force for the mass transport of a component from one phase to the other is given by the difference in its electrochemical potential in the two phases, and it is generated by changes in temperature, pressure, activity, or electrical potential. The hydrostatic pressure gradient across the membrane is negligible in MCr to avoid wetting while the electrical gradient does not hold, so that the driving force of the process is the partial pressure difference across the membrane, established by a temperature or activity difference between the two contacted solutions. In the case of a driving force generated by a temperature gradient, the system is named thermal membrane crystallizer; when the driving force is obtained by an activity gradient, generated by a difference in ionic strength, the system is named osmotic (or isothermal) membrane crystallizer.

Under the action of the driving force, solvent molecules migrate, in vapor phase through the porous membrane structure, from the site where their chemical potential is higher toward the lower chemical potential subsystem, thus generating supersaturation and, hence, nucleation and crystal growth in the crystallizing solution. The specific mechanism for mass transport depends on the operational configuration of the membrane crystallizer. Two cases exist: (1) solvent evaporation membrane crystallizer (thermal or isothermal) in which solvent is removed in vapor phase from the crystallizing solution and (2) antisolvent membrane crystallizer where an antisolvent is dosed inside the crystallizing solution by means of the membrane. Static (quiescent) and dynamic process can be performed. In the first case, the feed and the distillate solutions are quiescent, while in the second case, those two solutions are circulated

in forced solution flow environment, generally in a condition of laminar flow.

Generally, in order to avoid wetting, hydrophobic membrane materials are preferred for aqueous feed solutions, while hydrophilic membranes can be used for oleophilic solutions. In the most common arrangement, the distillate side of the membrane consists in a condensing fluid, often the pure solvent, at a lower temperature than the feed side in the case of thermal activation of the driving force, or in a stripping solution consisting in a hypertonic solution of inert salts (NaCl, MgCl₂, CaCl₂, etc.) in the case of the isothermal configuration.

While for the crystallization of inorganic substances or low molecular weight organic compounds, the thermal system can be affectively used, for the crystallization of heat-sensitive molecules, like proteins, the osmotic configuration appears more appropriate tank to its milder operating conditions (Curcio et al. 2001).

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Solvent Swollen Polymer

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Swollen polymers are classically named as gels, although the nature of the dissolved solvent allows distinguishing between three main classes of compounds: aerogel or xerogel when the network spaces are full of air, hydrogel, and organic gel when embedding water or oil. The swelling is defined as a penetration of a solvent into the polymer network that causes an abrupt change in the

volume (Gugliuzza and Drioli 2007), moving the boundary from unsolvated glassy region to solvated and expanding rubbery domain. This event occurs when there are unbalanced osmotic forces and viscoelastic restoring forces, while it is stopped when these forces reach the equilibrium. The opposite event is when the solvent releases from the polymer matrix, thereby causing deswelling.

Both the neutral and ionic polymers can swell, and different forces can take place during expansion, such as hydrophilic/hydrophobic and/or ionic interactions. The degree of crystallinity, cross-linking, as well as the strength of attractive and repulsive forces can seriously affect the intensity of the swelling (Flory and Rehner 1943).

Thermodynamically, the behavior of a swollen polymer can be described by the total free energy (ΔG_{total}), expressed as the sum of the free energy of mixing (ΔG_{mix}) and the elastic free energy (ΔG_{el}). An additional energetic term, such as the ionization free energy (ΔG_{ion}), must be also included when the polymer is a polyelectrolyte. Kinetically, the swelling event can be studied on the basis of the solvent diffusion rate and can be classified as Fickian or non-Fickian depending on the polymer chain relaxation (Crank and Park 1951). In a Fickian diffusion, the solvent rate is usually slower than relaxation rate of the segment chains (Case I transport), while in a non-Fickian diffusion, the solvent moves quicker than chain relaxation (Case II transport) or with a comparable rate (anomalous transport) (Berens and Hopfenberg 1978).

A somewhat simplified and empirical equation to study the diffusion through the polymers is

$$\frac{M_t}{M_\infty} = kt^n \quad (1)$$

where M_t and M_∞ are the mass uptake at time t and equilibrium, t and n are constants related to polymer-solvent systems. The type of diffusion can be established from the diffusional constant n . Value equal to 0.5 indicates Fickian diffusion; $0.5 < n < 1.0$ values are typical of anomalous transport, while values equal to 1 are estimated for Case II transport.

Better models have been proposed to study the non-Fickian diffusion. The following relation has been, for example, proposed for systems wherein M_t/M_∞ ratio is 0.60 (Crank and Park 1951):

$$\frac{M_t}{M_\infty} = (1 - Ae^{-k_2 t}) \quad (2)$$

A is a constant and is calculated together with k_2 from the slopes and intercepts of the plot of $\ln(1 - M_t/M_\infty)$ versus time t at times later than those corresponding to $M_t/M_\infty = 0.60$.

Instead, relation 3 well describes the anomalous transport:

$$\frac{M_t}{M_\infty} = k_1 t + k_2 t^{\frac{1}{2}} \quad (3)$$

where $K_1 t$ expresses the relaxation-controlled process, while $k_2 t^{1/2}$ quantifies the dependence of the transport on diffusion.

A discontinuity of the volume transition can be observed in many gels, thereby leading the polymer from a swelled to a shrunk state and vice versa, depending on the predominance of unbalanced hydrophobic/hydrophilic and/or ionic forces. Formation or destruction of hydrogen bonding as well as the interactions with counterions in specific chemical environments can decide the expansion or the collapse of the polymer network, making smart gels/membranes whereby a transport phenomenon can reversibly be controlled (Chaterji et al. 2007; Diaconu et al. 2012).

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Solvent-Resistant Nanofiltration

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Synonyms

Organic solvent nanofiltration (OSN)

Solvent-resistant nanofiltration (SRNF) is a pressure-driven technique to realize separations up to the molecular level in solvent streams (Vandezande et al. 2008). Small solvent molecules will permeate through the membrane, while solutes (with a molecular weight between 200 and 1000 Da) will be retained. Applications are widespread and mainly found in the (petro) chemical, pharmaceutical, and food industry. A good SRNF membrane is characterized by an excellent performance (high flux as well as high selectivity); long-term mechanical, chemical, and thermal stability; low fouling tendency; and a cost-effective and defect-free production.

Both ceramic and polymeric membranes can be applied in SRNF. Ceramic membranes are often synthesized from alumina, zirconia, or titania. Considering chemical, thermal, and physical stability, these membranes are most robust. They are able to combine a good selectivity with a long lifetime. However, ceramic membranes are expensive due to a complicated large-scale production process, rather brittle and intrinsically hydrophilic (low flux in apolar solvents unless surface treated). Therefore, polymeric membranes are considered to be the most interesting material

Solvent-Resistant Nanofiltration, Table 1 Suppliers of commercial SRNF membranes and their products (as in October 2012)

Company	Membrane	Material	Stability range	MWCO
Evonik (Germany) ^a	DuraMem [®]	Lenzing P84 [®] polyimide (*cross-linked)	Acetone, ethanol, methanol, tetrahydrofuran, dimethylformamide*, dimethyl sulfoxide*, dimethylacetamide*, isopropanol, acetonitrile, methyl ethyl ketone, ethyl acetate, and more	150–900 Da
	PuraMem [®]	Lenzing P84 [®] polyimide	Toluene, heptane, hexane, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, and more	280–600 Da
SolSep BV (the Netherlands) ^b	SolSep UF	Diverse (unspecified)	Alcohols, aromatics, esters, ketones, chlorinated solvents	10,000–20,000 Da
	SolSep NF	Diverse (unspecified)	Methanol, ethanol, propanol, acetone, ethyl acetate, hexane, toluene, chlorobenzene	300–750 Da
Borsig Membrane Technology (Germany) ^c	GMT-oNF	PDMS-based composites	Alkanes, alcohols, aromatics, ethers, esters, ketones	Unspecified
Inopor [®] (Germany) ^d	Inopor [®] nano	TiO ₂ , SiO ₂	Unspecified	450–750 Da

^a<http://duramem.evonik.com/product/duramem-puramem/en/Pages/default.aspx>^b<http://www.solsep.com/>^c<http://mt.borsig.de/>^d<http://www.inopor.com/en/index.html>

for SRNF applications. Advantages are the large variety of available polymers, their relatively low price, and the ease of processing and upscaling. An important issue with polymeric membranes is their limited thermal and chemical stability. Interactions between organic solvent and membrane can cause these membranes to swell extensively (or even dissolve) resulting in loss of selectivity. Cross-linking of the membrane matrix is often performed to increase the polymer stability in strong solvents (e.g., dimethylformamide). Cross-linking can be achieved chemically, thermally, or by irradiation (UV, plasma). Typical cross-linked polymers for SRNF are polyimide, polydimethylsiloxane, and polyacrylonitrile.

Polymeric membranes mostly have an asymmetric structure consisting of a thin, dense top layer on a porous support. They can be divided into two categories: integrally skinned and composite materials (Peeva et al. 2010). The first are synthesized via phase inversion, in which a polymer film is transformed from a liquid to a solid state in a controlled manner. The latter consist of two different materials, where the porous support

is often prepared via phase inversion, while the dense layer is put on top via a different technique (e.g., dip or spin coating, interfacial polymerization, grafting).

Transport through SRNF membranes is complex due to the interactions between solvent, solute, and membrane (e.g., swelling). Two models are often applied to describe the transport mechanism but also the combination of both appears. For loose SRNF membranes, the pore-flow model is used while the solution-diffusion model is applied for dense SRNF membranes. Both take into account membrane properties, which can vary depending on the feed characteristics. This implies that the same membrane can behave as loose in one solvent and as dense in another solvent.

Currently, only a limited number of companies supply commercial SRNF membranes (listed in Table 1). In the past, Koch Membrane Systems (USA) was another producer of SRNF membranes (MPF series), but they ceased their SRNF production. Together with StarMem (MET-Evonik, previously Membrane Extraction Technology), the MPF membranes were the first

commercially available SRNF membranes, making them the subject of many studies. Evonik, SolSep, and Borsig offer polymeric membranes in flat sheet form or spiral-wound modules. Inopor supplies ceramic mono- and multichannel tubes.

Cross-References

► [Organic Solvent Nanofiltration \(OSN\)](#)

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SO_x, Effect on Membrane Properties

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The combustion of sulfur-containing fuels, such as coal, results in the production of SO₂ and SO₃, commonly collectively referred to as SO_x. The typical coal-fired power station flue gas has SO_x concentrations between 1000 and 5000 ppm in their untreated flue gas, dependent on the sulfur content of the coal, of which the main component is SO₂. The contribution of SO_x to acid rain has meant that their emissions have been heavily regulated for over 30 years. The similar chemical properties between SO_x (in particular SO₂) and CO₂ also correlate into the behavior of SO_x in membrane separation processes.

The high molecular weight of SO₂ and SO₃ relative to other components of flue gas means that for Knudsen diffusion-based membranes, the SO_x components will remain in the retentate.

SO_x, Effect on Membrane Properties, Table 1 SO₂ permeabilities (barrer) and SO₂/CO₂ selectivity in a range of polymeric membranes

	SO ₂ permeability	SO ₂ /CO ₂
Cellulose triacetate	270	48
Polyacrylate	1,700	41
Polyethylene glycol	4,100	44
Polyamide-6-b-ethylene oxide	1,000	7.6
Polytetrafluoroethylene-co-ethylene	2.6	1.32

Similarly, the large kinetic diameters of SO₂ and SO₃, both greater than CO₂, means for molecular sieve based membranes the SO_x components of flue gas will leave the membrane module mainly in the retentate stream (Scholes et al. 2009). However, SO₃ and to a less extent SO₂ are strongly condensable gases, much greater than CO₂. Hence, for surface diffusion and capillary condensation separation, it may be possible for porous membranes to be selective for SO_x.

Solution diffusion-based nonporous membranes have been studied for SO_x separation, because of membrane research in the 1970s on desulfurization of flue gas. A list of polymeric membrane SO₂ permeabilities are provided in Table 1, along with SO₂/CO₂ selectivity. The majority of polymeric membranes show SO₂ selectivity, because of the stronger condensability of SO₂ (Felder et al. 1975). The relationship between SO₂ permeability and SO₂/CO₂ selectivity follows a typical Robeson upper bound plot. To date no permeability data has been reported for SO₃ through a nonporous membrane. This is probably because pure SO₃ is a liquid at room temperature and experimentally difficult to handle. However, given the strong condensable state of SO₃ compared to SO₂ and CO₂, it is reasonable that SO₃ will experience a greater permeation through glassy polymeric membranes than either SO₂ or CO₂.

SO₂ is a known plasticizer of polymeric membranes, producing a more rubbery material and increasing the diffusivity of penetrants. Its plasticizing effect is believed to be stronger than CO₂, though this has only been confirmed for

polyvinylidene (Zavaleta and McCandless 1976). In many industrial processes where SO_x is present, there exist high levels of water vapor. This allows for the generation of sulfuric acid, which results in membrane degradation. For example, cellophane-based membranes experience a 30-fold increase in SO₂ permeability when water is present, associated with increased free volume within the membrane because of acidic degradation (Hanousek and Herynk 1962). The fact SO₃ is a liquid at ambient temperature means it is very likely to have the same plasticization and degradation effect on polymeric membranes as SO₂.

$$\begin{aligned} \min_x \quad & f(x) \\ \text{s.t.} \quad & h(x) = 0 \\ & g(x) \leq 0 \end{aligned}$$

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Spacer Arm Length

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The spacer arm length refers to the length of hydrocarbon chain between the solid support and the functional ligand.

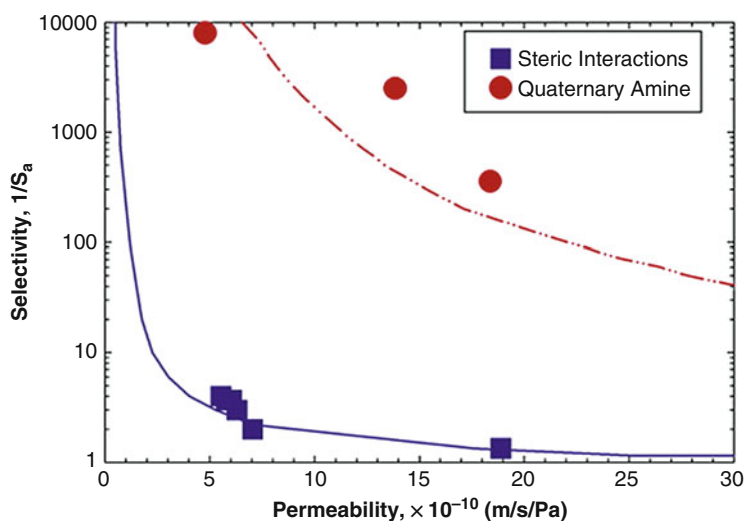
For ion exchange and affinity chromatography/membrane, studies have demonstrated that the spacer arm length can affect the overall system performance. In general, when the immobilized

ligand is a small molecule, such as a receptor substrate or a chemical antigen, steric hindrance occurs between the immobilization support and the substance to be isolated. This phenomenon may cause a reduction or complete lack of specific binding (Zou et al. 2001). To overcome this problem, it is often necessary either to select a different support (i.e., one with a spacer arm already attached) or to bind a spacer molecule to the support prior to attaching the ligand. An optimal spacer arm ensures that the functional groups are placed a suitable distance from the surface of the solid support and are easily accessible to the macromolecules. An ideal spacer arm should have (1) proper length (at least three atoms), (2) no active center that could cause nonspecific adsorption, and (3) at least two functional groups, one to react with the base support and one to serve as the chromatographic ligand (Zou et al. 2001).

For charge-modified membranes with different spacer arm lengths, recent researchers demonstrated that the spacer arm length can have a strong effect on the performance characteristics of electrically charged membranes by electrostatic exclusion effects. Even though the hydraulic permeabilities of these membranes were essentially identical, membranes with larger spacer arm length have greater retention of a like-charged molecule. The greater retention with larger spacer arm length is directly related to the effective surface charge or apparent zeta potential (Rohani and Zydney 2010; Shao et al. 2013). The permeability-selectivity trade-off plot for the charge-modified membranes with different spacer arm length demonstrated that the electro-static interactions led to much better ultrafiltration performance of enhanced selectivity and permeability than could be obtained with conventional (neutral) membranes. Figure 1 shows a plot of the selectivity (or separation factor) as a function of the permeability for cytochrome c for unmodified and positively charged versions of composite regenerated cellulose ultrafiltration membranes. The format for plotting the data is analogous to the classical Robeson plot used to analyze the behavior of gas separation membranes. High-performance membranes would lie in the upper right hand corner of the plot, having both large selectivity and large

Spacer Arm Length,

Fig. 1 Permeability-selectivity trade-off for cytochrome c using unmodified and positively charged Ultracel™ membranes. The solid and dashed curves represent model calculations for an uncharged membrane and a positively charged membrane consisting of a parallel array of cylindrical pores with a log-normal pore size distribution (Rohani and Zydney 2010)



permeability. Unmodified and po. For example, at a hydraulic permeability of about 6.0×10^{-10} m/s/Pa (15 L/m²/h/psi), the selectivity for the positively charged membrane is more than three orders of magnitude larger than that of the unmodified membrane. The charge-modified membranes with different spacer arm lengths can be well exploited to enhance the performance of ultrafiltration processes for real applications. Mehta and Zydney (2008) generated a series of positively-charged membranes with different spacer arm length by activation of base cellulose membrane with epichlorohydrin followed by reaction with diamines having different numbers of alkyl groups between the two amines. Experimental data showed that at low ionic strength (5 mM), the observed sieving coefficient for cytochrome c through the 30 kDa membrane made with 1,10-diaminodecane ($n = 10$) was more than an order of magnitude smaller than that for a similar membrane made using 1,2-diaminoethane ($n = 2$) even though these membranes had very similar hydraulic permeabilities and pore size distributions, where n is the number of alkyl groups between the amine functionalities. This large reduction in the protein sieving coefficient was found to be consistent with the observed increase in the membrane zeta potential, which was most likely due to the increase in net charge associated with the reduction in electrical

interactions between the two amine groups in the diaminodecane in combination with the greater displacement of the charge functionality into the interior of the membrane pore for the larger ligand. Later, Shao et al. (2013) generate a series of negatively charged ultrafiltration membranes that differed in spacer arm length by covalent attachment of negatively charged group to a commercially available regenerated cellulose membrane. Results indicated that the membrane with larger spacer arm length has better rejection of humic acid and less membrane fouling compared to that with smaller spacer arm length, which is also consistent with the larger charge of the membrane having larger spacer arm length.

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Spacer-Filled Channels

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Spacer-filled channels refer to the use of feed channel spacer in flat sheet and spiral-wound membrane processes. Feed channel spacer is an essential part in spiral-wound module to separate membrane leaves (Fig. 1). There are many different types of feed spacers in the market, but the most commonly used feed spacers are ladder and diamond type (Fig. 2). They differ in the orientation of the spacer in touch with the flow direction. Feed spacers are usually made of plastic polypropylene (PP). The opposite of spacer-filled channel is called empty channel in which simply no spacer is placed on top of the membrane.

One of the most important geometric characteristic of spacers is spacer voidage (ε), which is a product of the mesh size (l_m), diameter of

filaments (d_f), spacer height (h_{sp}), and angle between filaments (θ) (Da Costa et al. 1994):

$$\varepsilon = 1 - \frac{\pi d_f^2}{2 l_m h_{sp} \sin \theta}$$

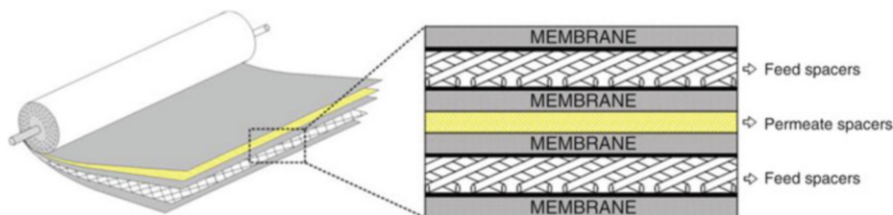
The presence of spacer reduces the average cross-sectional area of the channel, which results in the correction of effective crossflow velocity (u_x) from original superficial crossflow velocity (u_v):

$$u_x = \frac{u_v}{\varepsilon}$$

where u_v is given by the total flow rate divided by the total cross-sectional area.

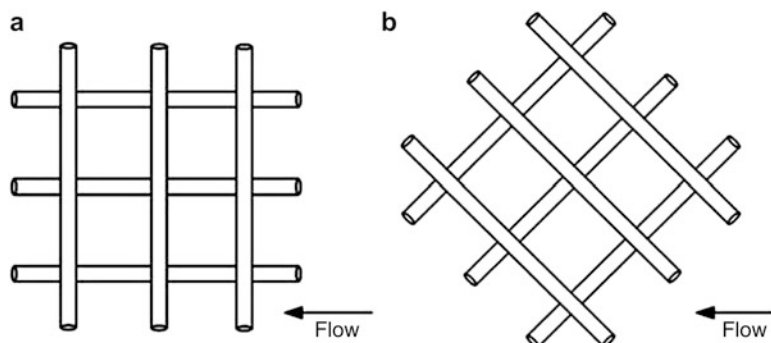
In reverse osmosis or nanofiltration processes, spacer filled channels provide better membrane performance than empty channels by lowering trans-membrane pressure (TMP) which is caused by the reduction concentration polarization (CP). CP is the exponential ratio of flux (J_v) and mass transfer coefficient (k_m):

$$CP = \exp\left(\frac{J_v}{k_m}\right)$$



Spacer-Filled Channels, Fig. 1 Spiral-wound module

Spacer-Filled Channels,
Fig. 2 Most common feed
channel spacers (a) Ladder.
(b) Diamond



k_m is greater in spacer filled channels than in empty channels. At constant flux membrane operation, the relationship between J_v , CP, and TMP is shown below:

$$J_v = \frac{TMP - CP \Delta \pi_w}{\mu R_m}$$

Where $\Delta \pi_w$ is the osmotic pressure difference between feed and permeate sides, μ is the solution viscosity, and R_m is membrane resistance.

In membrane operations which rely on temperature difference (e.g., direct contact membrane distillation), temperature polarization – temperature difference between bulk and on the membrane surface – causes significant loss to the thermal driving force (Phattaranawik et al. 2003). Feed spacers help to reduce temperature polarization by increasing heat transfer and further results in higher permeation flux.

The disadvantage of spacer feed channels is the elevated channel pressure drop (ΔP). ΔP is very sensitive to crossflow velocity (u_x) where spacer causes flow blockage and increases u_x :

$$\Delta P_{CH} = \frac{\rho u_x^2}{2} \cdot \frac{A'}{\text{Re}^n} \cdot L_{CH}$$

where ρ is solution density, L_{CH} is channel length, Re is Reynolds number, and A' is constant.

Increased mass transfer coefficient in spacer-filled channels provides reduction to the rate of membrane fouling. Effectiveness of spacer toward fouling reduction has been tested on colloids, protein (Schwinge et al. 2000), and biofouling (Suwarno et al. 2012). In biofouling however, presence of spacers may also be problematic as biofilm may grow on the spacers and increase channel pressure drop (Vrouwenvelder et al. 2009). One must note that spacers do not completely stop fouling. In fact, in some situation spacers may provide several dead zones which may cause deposition of high level of foulants. Selection of suitable type of spacer configurations (voidage, size, etc.) to reach optimal operations is dependent on operating conditions (crossflow velocity, feed type, etc.).

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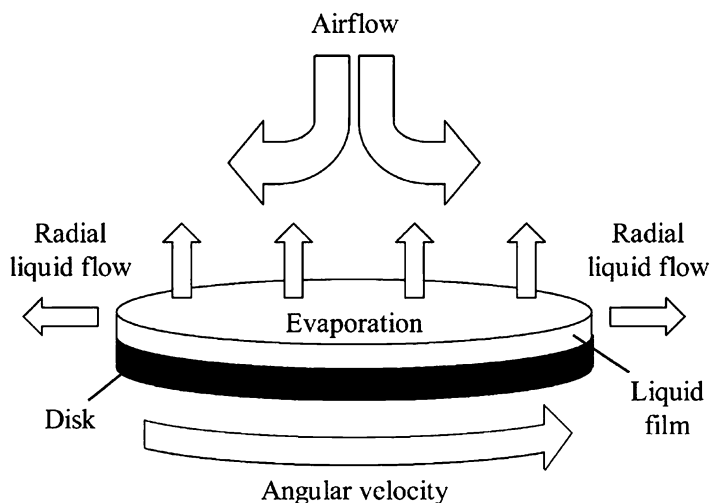
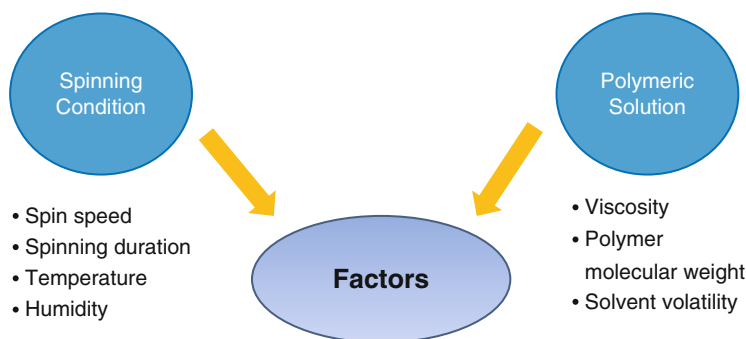
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Spin Coating

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The technique of spin coating is widely used in many industrial processes, in particular microelectronics industry to apply a uniform photoresists and photolithographic film onto silicon wafers. This coating technique is also used in the preparation of composite membrane but only at the laboratory scale. It is reported that the membranes prepared by spin-coating technique could have thicknesses in the range of 0.5–30 μm (Baker 2012; Wang et al. 2011) which is significantly thinner than those of membranes made of casting technique using knifelike tool, i.e., between 80 and 250 μm . Since membrane is a pressure-driven process, the thinner the membrane layer, the lower the transport resistance of water which as a consequence can lead to greater water permeability. However, it must be pointed out that spin coating is limited to flat substrates, which limits its

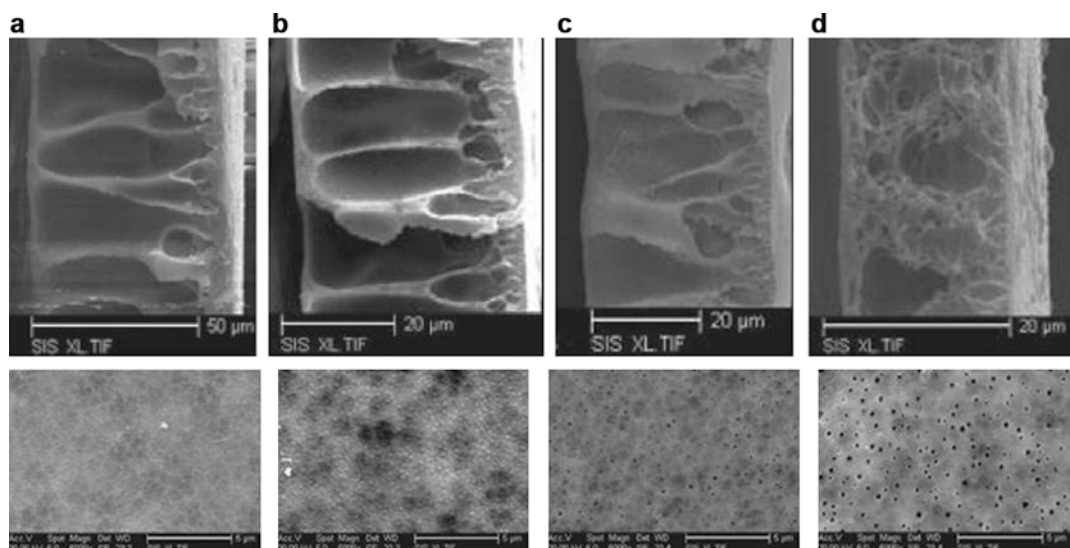
Spin Coating,**Fig. 1** Schematic of a spin-coating process (Norrman et al. 2005)**Spin Coating,****Fig. 2** Factors affecting the membrane properties during spin-coating process

applicability on the circular-shaped objects such as hollow fiber and tubular membranes.

Figure 1 illustrates a schematic of a lab-scale spin coater (also known as spinner). Prior to spin coating, an excess of polymeric solution is applied to the center of the circle plate made of either glass or stainless steel material. It is followed by rapid acceleration of the plate to the desired rotation rate (angular velocity) at a given duration of spinning. In the spin-coating process, polymeric solution flows radially due to the action of centrifugal force, causing the excess solution ejected off the edge of the plate. As the solvent used to dissolve polymer is volatile, an ultrathin layer of film is thus produced on the plate surface due to a dramatic rise in film viscosity caused by solvent evaporation. After coating process, the nascent membrane together with the plate is immersed into water coagulation bath in which phase

inversion takes place and a membrane is produced. The resulting membrane is further immersed in another water bath for another day in order to completely remove the residual solvent from membrane prior to use.

There are many factors governing the thickness and morphology of the membrane produced via spin coating. As shown in Fig. 2, the properties of the membrane prepared from spin coating can be affected by both polymeric solution and the spinning conditions. For instance, the thickness of film increases with decreasing spin speed or decreases with decrease in viscosity of solution (Norrman et al. 2005; Hall et al. 1998). The solution viscosity is in general dependent on the polymer concentration and type of polymer used in the preparation of solution in which the higher the polymer concentration and the higher the molecular weight of polymer used in the solution



Spin Coating, Fig. 3 Cross section and top-surface morphologies of the membranes prepared from different spinning times with spin speed of 3,000 rpm, (a) 60 s, (b) 120 s, (c) 180 s, and (d) 240 s (Wang et al. 2011)

preparation, the greater the viscosity of solution produced. Increase in spinning time on the other hand has potential to produce thinner membrane with more visible pores on the surface. It is reported in the work of Wang et al. (2011) that the polyvinylidene fluoride (PVDF) membrane layer tended to become thinner, while its surface pore became more visible with increasing spinning time from 60 to 240 s as shown in Fig. 3. It must be also noted that at prolonged spinning time (240 s), the cross-sectional structure of the membrane became more porous and disordered which could be the result of the evaporation-induced phase separation instead of nonsolvent (water)-induced phase separation.

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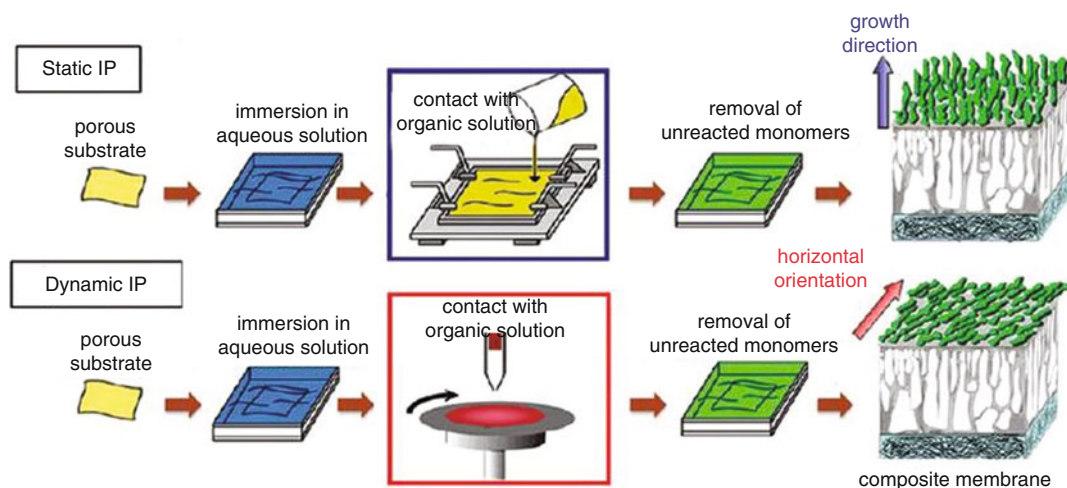
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Spin Coating Interfacial Polymerization (IP) Techniques

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The use of spin coating interfacial polymerization (IP) technique in the preparation of thin-film composite membrane is rarely been reported in the literature, although it involves very similar procedure as the conventional IP technique. As illustrated in Fig. 1, it can be seen that instead of pouring organic solution directly on the surface of substrate containing amine monomer, the organic solution is spin coated over the substrate surface using the spin coating IP technique which is also known as dynamic IP. Owing to rapid acceleration of the spinning plate to the desired rotation rate, a powerful centrifugal shearing force is created which spreads away the organic solution from the axis of rotation toward the substrate outer edge. Because of this, it results in the IP reaction between the acyl chloride monomer in the organic solution and the amine monomer on



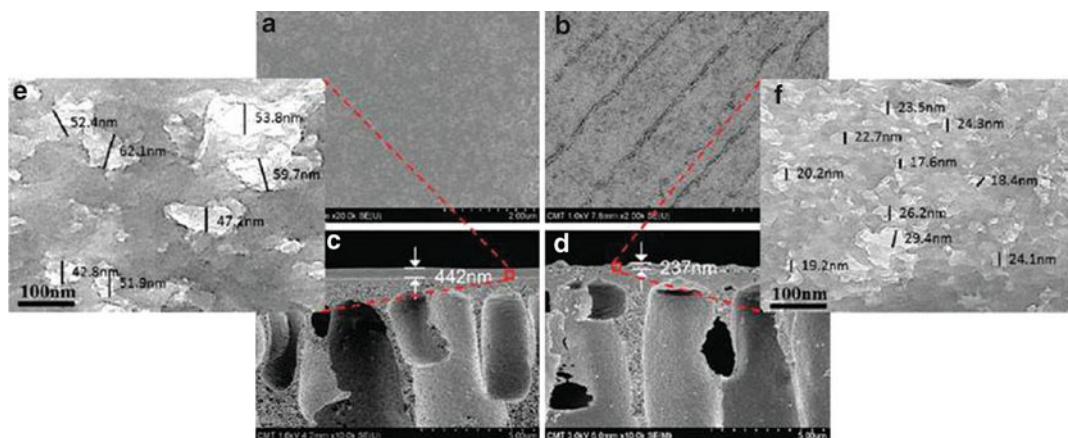
Spin Coating Interfacial Polymerization (IP) Techniques, Fig. 1 Preparation of thin-film composite polyamide membranes through different interfacial polymerization (IP) techniques, (a) static IP (conventional IP) and (b) dynamic IP (spin coating IP) (Reprinted (adapted) with permission from (An Q, Hung

WS, Lo SC, Li YH, Guzman MD, Hu CC, Lee KR, Jen YC, Lai JY (2012) Comparison between free volume characteristics of composite membranes fabricated through static and dynamic interfacial polymerization processes, *Macromolecules* 45: 3428–3435). Copyright (2012) American Chemical Society)

the substrate surface, creating a very thin polyamide (PA) layer on the top of the substrate with good uniformity. It is also reported that by using this dynamic IP technique, molecular chains are oriented in the horizontal direction and stacked up closer to one another in comparison to the vertical growth direction found in the conventional IP technique (An et al. 2012). Conventional IP is static which allows amine and acyl chloride monomers to contact each other and stand for some time before a polymer film is formed at the interface between aqueous and organic solution.

Similar to the typical spin coating process (Norrman et al. 2005; Wang et al. 2011), there are several variables that have influential role in affecting the properties of PA layer formed during spin coating IP process. These include spinning speed, spinning duration, temperature, and humidity. In addition to this, the organic solution properties which depend on the factors such as type of monomer and its concentration as well as solvent volatility might also have the potential to affect the cross-linking degree of PA structure (Lau et al. 2012).

Figure 2 compares the top and cross-sectional structures of the thin-film composite PA membranes prepared from two different IP techniques. With respect to the thickness of PA layer, it is found that the composite membrane prepared from spin coating IP technique has a significantly thinner selective layer than that of a membrane made of conventional IP technique. Furthermore, the spin-coated PA layer possesses smaller cavities as evidenced on the cross-sectional image of TEM. This phenomenon is mainly due to the minimum amount of water left within the PA film because water is significantly drawn out during spinning process due to the powerful centrifugal force. The water (in the PA matrix) then evaporates during drying and leaves behind small cavity as explained by An et al. (2012). In addition, several parallel lines are clearly observed on the spin-coated PA layer which is most likely due to the rotation effect of spinning, creating wavy fluid flow pattern on membrane surface. The presence of parallel lines is believed to cause the membrane surface roughness to increase, resulting in different membrane separation performances. It must be pointed out that the integration



Spin Coating Interfacial Polymerization (IP) Techniques, Fig. 2 Micrographs of thin-film composite PA membranes fabricated through conventional (a, c, e) and spin coating (b, d, f) IP processes. For spin coating IP, spin coating rate = 6000 rpm. (a–d) SEM surface and cross-sectional images; (e, f) TEM cross-sectional images (Reprinted (adapted) with permission

from (An Q, Hung WS, Lo SC, Li YH, Guzman MD, Hu CC, Lee KR, Jen YC, Lai JY (2012) Comparison between free volume characteristics of composite membranes fabricated through static and dynamic interfacial polymerization processes, *Macromolecules* 45: 3428–3435). Copyright (2012) American Chemical Society)

of IP technique with spin coating process is advantageous in preparing unique structure of PA layer which is difficult to achieve using conventional IP technique.

Spiral Wound Membrane Module

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Synonyms

[Spiral wound membrane](#); [Spiral wound module](#)

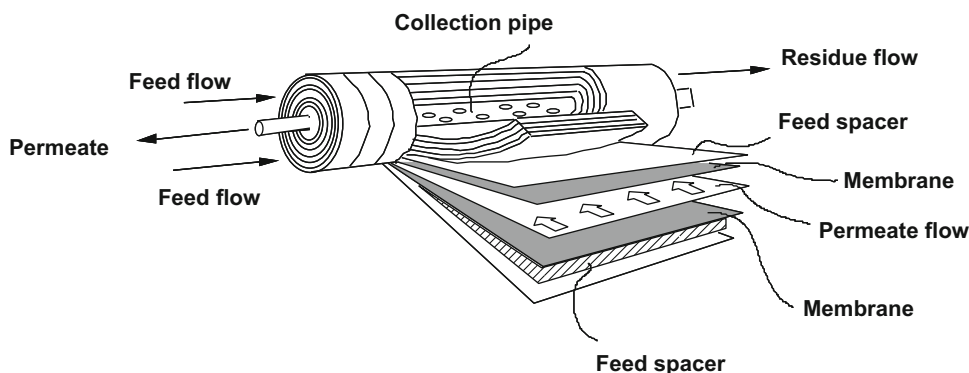
A number of membrane module designs are possible, and all are based on two types of membrane geometry: (i) flat sheet membranes and (ii) capillary fibers. Plate-and-frame as well as spiral wound modules house flat membranes (Mulder 1997).

The spiral wound module is an important module type for membrane applications. Initially it was developed for reverse osmosis applications and is nowadays also used in ultrafiltration and gas permeation applications (Blackmer and Hedman 1979).

Spiral wound modules are used where pressure drop has to be considered and when counter current flow is not needed to maximize separation efficiency. Higher pressure applications involving costly pressure vessels and piping make the hollow fiber

Spiral Wound Membrane

► [Spiral Wound Membrane Module](#)



Spiral Wound Membrane Module, Fig. 1 Schematic drawing of a spiral wound module taken from Scholz et al. (2011)

modules more favorable because this reduces the component costs of the system by as much as a factor of ten in some cases (Koros and Fleming 1993).

The spiral wound module is the next logical step from a flat membrane. It is in fact a plate-and-frame system wrapped around a central collection pipe, similar to a sandwich roll. Feed and permeate-side spacer material is glued along three edges to build a membrane envelope. A feed-side spacer is separating the top layer of two flat membranes simultaneously acting as a turbulence promoter (Fig. 1; Mulder 1997).

The feed flows in axial direction over the envelopes built up by two membrane stacks. The permeate is collected on the inside of the envelope and spirals into the central permeate collection pipe. The packing density of this module ($300\text{--}1,000\text{ m}^2/\text{m}^3$) is greater than that of the plate-and-frame module but strongly depends on the channel height, which in turn is determined by the thickness of the permeate and feed-side spacer material (Mulder 1997). The spacer is not only used to keep the distance between the membranes, but it also enhances the mass transfer at a minimum pressure drop (Blackmer and Hedman 1979). Net-type spacers are common for spiral wound modules. Important characteristics determining the module performance influenced by this type of spacer are:

- Filament diameter
- Hydrodynamic angle
- Mesh size

- Voidage
- Position to flow (transverse)

The analysis of pressure drop within spacer-filled channels can be found in Baker et al. (2010). Recently a double helix spacer with enhanced mass transfer characteristics combined with a reduced pressure drop was developed at RWTH Aachen University (Feng and Ivory 2000).

Several (up to 6) spiral wound modules are assembled in one pressure vessel and are connected in series via the central permeate tubes (Fig. 2; Mulder 1997; Blackmer and Hedman 1979). New vessel designs currently emerge that addresses the huge gas flows to be potentially treated in post combustion CO_2 capture (Bao and Lipscomb 2002).

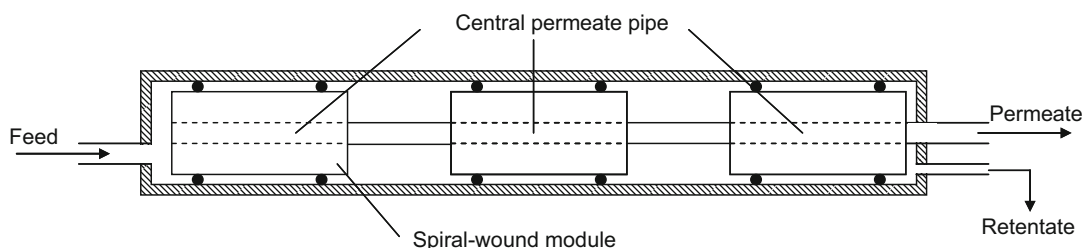
The advantages of spiral wound modules are the following (Caro et al. 2007):

- Simple, cost-effective construction
- Relatively high packing density/membrane area to volume ratio (up to $1,000\text{ m}^2/\text{m}^3$)
- Good mass transfer due to feed spacer

The disadvantages are the following:

- Long permeate path
- Difficult to clean

In total up to 20 % of the commercial gas separation membranes are being formed into spiral wound modules (Baker 2002).



Spiral Wound Membrane Module, Fig. 2 Schematic of a pressure vessel containing three spiral wound modules in series taken from Scholz et al. (2011)

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Spongelike Structure

Tao He

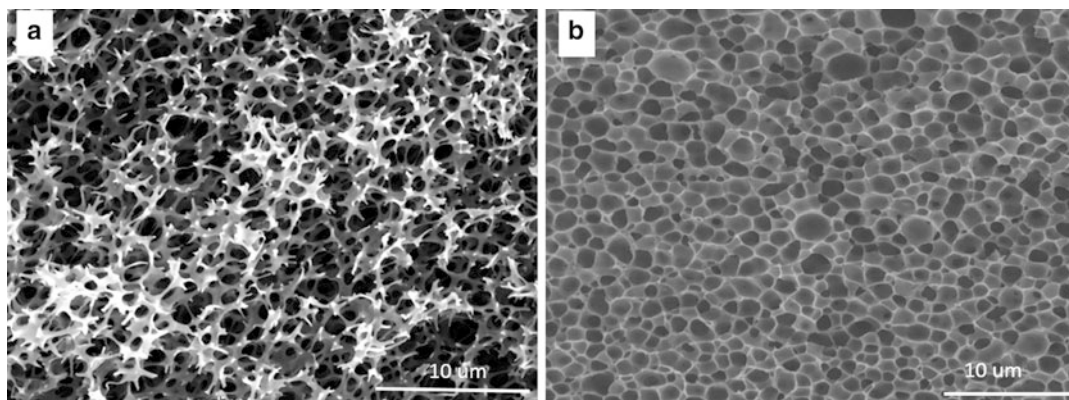
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Spongelike structure is a common membrane sub-layer morphology as shown in Fig. 1. Two types of spongelike structure may be identified: an interconnected network type (Fig. 1a) and a closed-cell type (Fig. 1b) characterized as individual separate cells. An ideal asymmetric membrane consists of a thin skin layer and an interconnected porous substructure. High interconnectivity, an important but difficult to be quantified property, of the porous substructure is crucial for low mass transport resistance. It is favorable due to the better mechanical properties than the fingerlike structure.

Formation of spongelike structure has the same origin as the fingerlike structure, liquid-liquid phase separation. Thermodynamically the liquid-liquid demixing of a polymer solution follows possibly two mechanisms: binodal demixing or spinodal demixing (Marcel 1996). In binodal demixing, once the nucleation of the polymer-lean phases is initiated, the growth of the nuclei proceeds until the net inflow of solvent or nonsolvent adjacent to the polymer-lean phases ends and/or the polymer-rich phases follow a glass transition (Li et al. 1996). In case of a crystalline polymer, a solid-liquid phase separation takes place; consequently, crystallization of the

Spiral Wound Module

► Spiral Wound Membrane Module



Spongelike Structure, Fig. 1 Spongelike structure of PES membranes. **a** Open-pore interconnected structure; **b** closed-cell structure

polymer-rich phases blocks the growth of the polymer-lean phases.

If the phase separation follows a spinodal demixing, myriads of polymer-lean phases are initiated at a short-time scale; the probability for the polymer-lean phases to get in touch with each other is high, leading to an open porous structure. For a semicrystalline polymer, closed pores may be opened up by an extra stretching step, followed by the solid-liquid demixing; thus a spontaneous demixing is not necessary. Some tips to prepare spongelike particularly interconnected porous structure include: (1) addition of pore-former additives (both small molecular weight and polymeric) (Boom et al. 1994), (2) selection of solvent/coagulant pair with strong interaction (to promote instantaneous demixing, thus favorable for spinodal demixing), and (3) decrease in the polymer concentration.

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Spray Coating

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Coating

A coating is applied to the surface of an object to protect it from environmental effects or to enhance its surface properties such as appearance, corrosion resistance, wear resistance, scratch resistance, adhesion, wettability, dielectric property, electrical conductivity, etc. The object to be coated may also be referred as substrate. In some cases, the coatings act as an essential part of the finished product such as in the case of semiconductor devices fabrication where the substrate material is silicon wafer.

Coatings may be applied as liquids, gases, or solids. “The coating which is applied on an object with a liquid spray is known as spray coating.”

Suspension and solution thermal spraying are the emerging methods of coating (Pawlowski 2009). Thermal spraying is a process that utilizes thermal energy to melt material in powder, wire, or rod form followed by providing kinetic energy to the molten or semi-molten material to propel it toward a prepared surface by expanding process gases. The impact of these molten or semi-molten particles on

the surface of substrate creates a coating buildup called spray coating. Thermal spraying could be achieved by various techniques including:

Plasma Coating

In plasma spray method, plasma gas such as argon/hydrogen or argon/hydrogen is heated by an arc between the two electrodes. This heating process causes expansion of plasma gas which accelerated through a shaped nozzle, creating very high velocity. Temperature of the plasma gas in the arc zone approaches about 20,000 K which remains up to 10,000 K even after exiting from the nozzle for several centimeters. This stream carries the coating material in molten form and applies to the substrate. Plasma spray coatings are commonly used in jet engines where it provides high-temperature protection to the parts which are exposed to combustion gases. This increases the life and efficiency of the system.

Electric-Arc Spray

An electric arc is created when two conductive wires carrying charges of opposite polarity meet in front of spray device. This electric arc melts the wires which are acting as feedstock for coating. Electric-arc spraying technique has the fastest coating rates among coating technologies. Flame or plasma is not involved in this coating technique which significantly reduces the heat transfer to the substrate material, making the process thermally efficient. The electric-arc spray is commonly used in the automotive industry and to coat large objects such as bridges with aluminum and zinc which provide corrosion resistance properties.

High-Velocity, Oxy-Fuel (HVOF) Coating

HVOF utilizes an extended nozzle to heat and accelerate the coating material. Typical HVOF devices operate at hypersonic gas velocities which provide kinetic energy helping to produce

dense and well-adhered coatings. HVOF coatings can be used for coating the high-tech medical devices and coating of carbide material to bolts used in agricultural machine which greatly extends the life of the bolt.

Flame Spray

Flame spray uses combustion of gases to melt powder, wire, or rod material and propels the molten droplets onto a surface to create a coating. Flame coatings are commonly used for materials requiring good wear resistance and excellent impact resistance such as agricultural harvesting components, oil-drilling parts, etc.

Cold Spray

Cold spray is technically not a thermal spray process since it does not use thermal energy as the primary energy source. In cold spraying, particles are accelerated to very high speeds by the carrier gas forced through a converging–diverging de Laval type nozzle. High-energy impact of feedstock solid particle causes plastically deformation of particles at substrate surface which subsequently bond metallurgically to the substrate to form a coating. The velocity is an important parameter to obtain such coating, and critical velocity value for bonding depends on the material properties such as nature of feedstock, powder size, and temperature. Some hard materials are also reported, but soft metals such as Cu and Al are best suited for cold spraying process (Seiji et al. 2008).

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Spray-Pyrolysis

► Perovskite Powder Preparation Methods

SPS/PES Asymmetric Blend Nanofiltration Membrane

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An SPS/PES asymmetric blend nanofiltration (NF) membrane is a novel semipermeable membrane used in nanofiltration process, such as water treatment for drinking water production, desalination, concentration, and purification and pharmaceutical and chemical industries. SPS/PES asymmetric blend nanofiltration membranes are developed in 2011 by Senuo Filtration Technology (Tianjin) Co., Ltd (Chen et al. 2011).

A nanofiltration membrane is a type of pressure-driven membrane with properties in between reverse osmosis (RO) and ultrafiltration (UF) membranes, with a membrane pore size between 0.5 and 2 nm, nominal molecular weight cutoffs from 200 to 1000 Da, and operating pressures between 5 and 40 bar (Hilal et al. 2004).

Most nanofiltration membranes are composite membranes produced via sophisticated fabrication processes, such as coating or interfacial polymerization, where the top selective layer and bottom porous substrate of the membrane can be independently modified and optimized (Lau et al. 2012; Mulder 2009). The fabrication processes for composite membrane in general involve various preparation conditions, making the entire process very labor intensive.

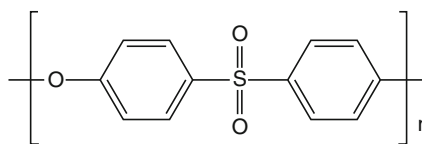
Asymmetric blend nanofiltration membranes are made by non-solvent-induced phase separation, which is a single-step process. Non-solvent-induced phase separation technology is a relatively simple preparation technique compared to composite membrane fabrication technology. And

also, the blending technique has the advantage of combining the positive features of each component while being very simple.

SPS/PES asymmetric blend nanofiltration membranes are fabricated by blending polyethersulfone (PES) with sulfonated polysulfone (SPS) as membrane material. PES is one of the important polymer materials in membrane fabrication, due to its excellent mechanical strength and thermal and chemical stability. PES also allows easy manufacturing of membranes, with reproducible properties and controllable size of pores down to several decade nanometers. Polyethersulfone repeating unit is shown in Fig. 1.

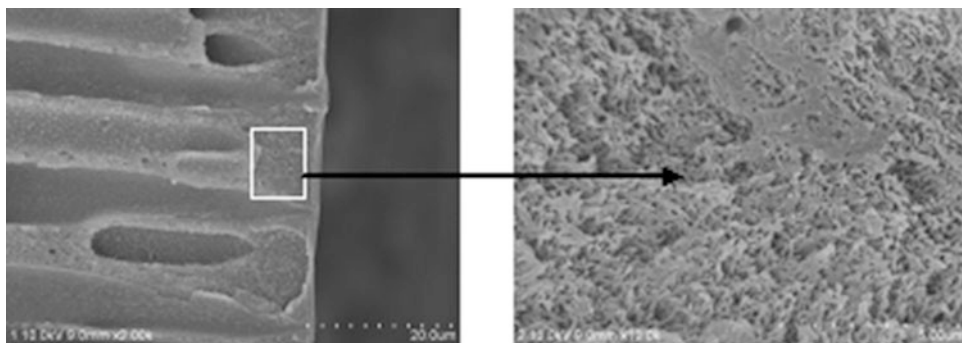
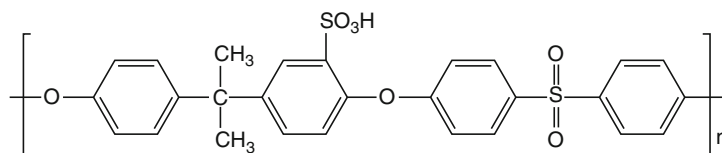
PES is also an inherently hydrophobic polymer. A wide range of evidence shows that membrane with adequate hydrophilicity can prevent deposition of many solutes such as protein, which can increase resistance to fouling. However, hydrophobicity of PES has limited its application in NF membrane preparations. Introducing sulfonic groups to membrane is an efficient way to improve the hydrophilicity of PES membrane, which can be carried out through the introduction of sulfonic groups directly into PES or by blending with another sulfonated material, such as sulfonated polysulfones (SPSs). Sulfonated polysulfone (repeating unit shown in Fig. 2) with hydrophilic group, sulfonic group, has adequate hydrophilicity. The high hydrophilicity can improve the water flux and pollution resistibility. But sulfonated polysulfones possess weak strength, which will cause bad stability for operation. The miscibility of PES with SPS is better enough. Sulfonated polysulfone can be induced to increase hydrophilicity of the PES nanofiltration membrane.

Besides increasing hydrophilicity, sulfonated polysulfone offers another advantage, negative



SPS/PES Asymmetric Blend Nanofiltration Membrane, Fig. 1 Polyethersulfone repeating unit

SPS/PES Asymmetric Blend Nanofiltration Membrane, Fig. 2 Sulfonated polysulfone repeating unit



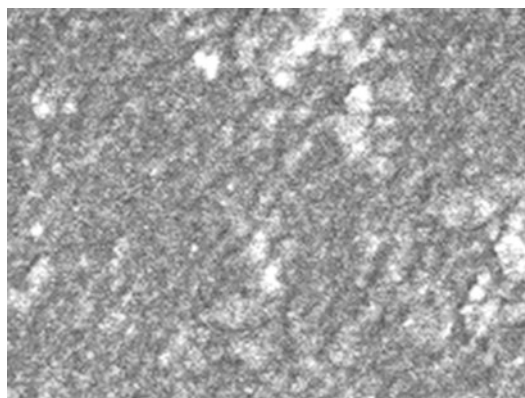
SPS/PES Asymmetric Blend Nanofiltration Membrane, Fig. 3 Typical cross section morphology of SPS/PES asymmetric blend nanofiltration membrane

charge. Membranes with fixed charges are predicted to exclude solutes or colloids bearing the same sign of charge and to decrease membrane fouling. SPS/PES asymmetric blend nanofiltration membranes with functional group, sulfonic group, can gain negative charges and give them great selectivity with respect to ions or charged molecules.

SPS/PES asymmetric blend nanofiltration membranes are primarily characterized by pure water flux, rejection, and hydrophilicity.

An SPS/PES asymmetric blend nanofiltration membrane is a combination of good hydrophilicity and mechanical strength, which can improve the water flux, antipollution ability, and stability of blend membrane. The negative charge due to sulfonic group leads to a high selectivity over ions or molecules with positive charges.

The SPS/PES asymmetric blend nanofiltration membrane has the asymmetric morphology, as shown in Fig. 3. Blending of PES with SPS in the casting dope leads to interesting asymmetric structure. There are fingerlike macropores and spongelike pores in SPS/PES membranes. A dense layer supported on a porous layer, as shown in Fig. 4.



SPS/PES Asymmetric Blend Nanofiltration Membrane, Fig. 4 Typical morphology of the top surface

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Stack of Single Cells in Electrodialysis

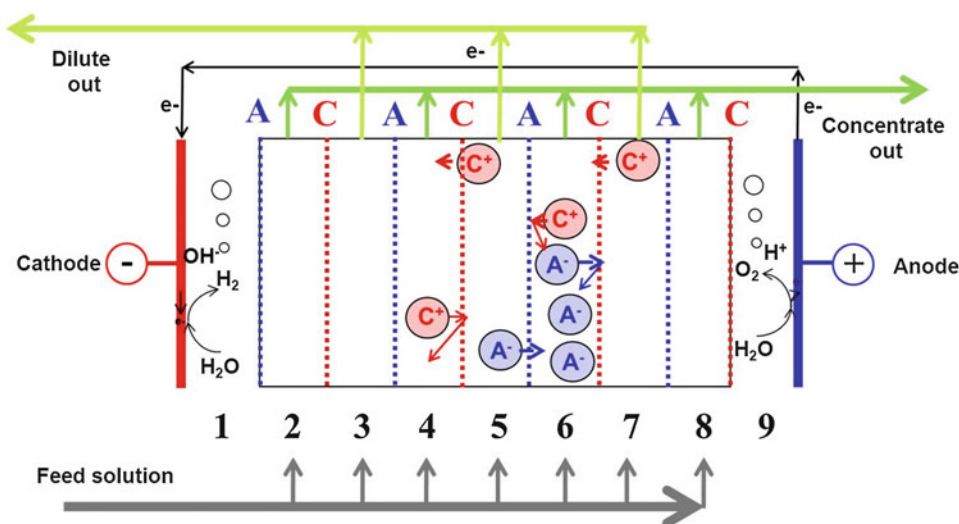
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Electrodialysis is an electrochemical process (see “► [Electrochemical Processing](#)”) for separating an aqueous feed solution into a concentrate or brine and dilute or desalted water by means of an electrical field and ion-selective membranes. Electrodialysis takes place in an electrodialysis stack. A schematic representation of such a stack with anion- (A) and cation- (C) exchange membranes arranged in an alternating series pattern is shown in Fig. 1. For practical application, number of membranes in an electrodialysis stack is much higher than shown in Fig. 1. For example, such stacks might contain up to 600 pairs of membranes (a unit cell is a combination of one cation-exchange membrane and one

anion-exchange membrane) (Seader and Henley 2006). The size of a membrane is usually between 0.4 and 1.5 m² and they are separated from each other by spacer gaskets. A typical voltage drop across the unit cell is 0.5–1.5 V and typical current densities are in the range of 5–50 mA cm⁻². The movement of ions in the electrodialysis stack is dictated by the direction of an electrical field and allowance of a membrane for an ion transport. For example, in compartments 3, 5, and 7 (Fig. 1) under influence of the electrical field cations will move across cation-exchange membrane and anions across anion-exchange membrane, resulting in formation of dilute. On the other hand, in compartments 2, 4, 6, and 8 the anion- and cation-exchange membranes do not allow movement of ions in the direction of electrical field, resulting in formation of concentrate in this compartments. As in other electrochemical processes, ionic current will be finally transformed into electrical current by means of electrochemical reactions taking place at the cathode and anode. The main application of electrodialysis is the desalination of brackish water. Other applications include waste water treatment, separation of salts, and some food industry applications.

Typical ion-exchange membranes are made of polystyrene, containing fixed sulfonate $-\text{SO}_3^-$ groups (cation-exchange membrane) or quaternary

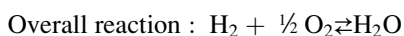
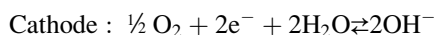


Stack of Single Cells in Electrodialysis, Fig. 1 Schematic representation of the electrodialysis process. C cation-exchange membrane, A anion-exchange membrane

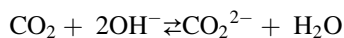
ammonium groups such as $-\text{NH}_3^+$ (anionexchange membranes) (2008). The thickness of the membranes is 0.2–0.5 mm and they are reinforced to provide better mechanical stability. The membranes are wetted with water, but due to the size of pore networks inside of membranes water transport across the membrane is largely prohibited. The selectivity of membranes for an anion or cation is better than 90 %.

Stack of Fuel Cells in Electrodialysis

Alkaline fuel cell (AFC) is a fuel cell type which utilizes alkaline electrolyte, usually potassium hydroxide. It consumes hydrogen and oxygen producing only water, heat, and electricity. Depending on a concentration of potassium hydroxide AFC can operate at temperatures between 60 °C and 250 °C. The fuel cell reactions are as follows:



The main ionic charge carriers are OH^- ions which mitigate from the cathode to the anode. Water is formed at the anode side and has to be removed from the system in order to prevent KOH dilution. The AFC has improved cathode performance compared to acidic fuel cells due to more favorable oxygen reduction reaction kinetics. For this reason, AFC can achieve higher efficiency, i.e., higher voltage at comparable current densities than other fuel cell types. It has very long operating life time, e.g., 15,000 h have been demonstrated (Cifraín and Kordesch 2003). Furthermore, alkaline conditions allow application of nonprecious metal catalysts which could reduce significantly the material costs of this fuel cell. One of the major disadvantages of AFC is its low CO_2 tolerance due to formation of carbonates according to:



The carbonates have low solubility in strong alkaline environments forming crystals, capable of blocking of electrolyte pathways. The low CO_2 tolerance and the application of liquid electrolyte are two main hurdles for the broader commercialization of these systems. However, due to its high efficiency and high power density AFC found applications in aerospace industry, e.g., they were employed on the Appollo missions as well as on the space shuttle orbitals. For other examples of developed AFC systems please see (Seader and Henley 2006; Electroseparations, electrodialysis 2008).

Hydrogen and oxygen gases in the AFC are separated by a membrane. Usually permeable membranes also called diaphragms have been used (Gülzow 2012). A common diaphragm material up to 1980s was asbestos which due to health and environmental concerns is nowadays abandoned. Alternative materials are different polymer materials like porous polyethylene plates, nonwoven polypropylene and similar. Potassium hydroxide electrolyte wets the diaphragm pores in order to ensure its ionic conductivity. For a good fuel cell performance, the electrolyte resistance induced by diaphragm has to be minimized. This resistance is influenced by the thickness of the diaphragm material, its pore size and tortuosity, and the KOH concentration. Since liquid electrolyte causes some practical problems in AFC usage, new developments go into direction of alkaline polymer electrolyte membranes which in addition to separation possesses, similar to its acidic equivalent (e.g., Nafion), ionic conductivity in absence of liquid electrolyte. Currently there is no long-term stable membrane functioning without a liquid electrolyte phase.

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Static Membrane Emulsification

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Static membrane emulsification (ME) refers to the formation of emulsion droplets by extruding the dispersed phase through the membrane pores into the continuous phase in the absence of surface shear (Fig. 1).

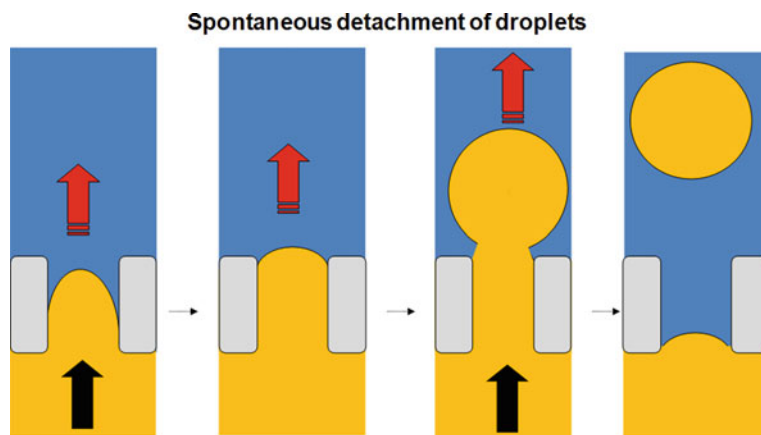
In the absence of shear flow at the membrane surface, the main forces acting on the droplets forming at the membrane pore level are (see Fig. 2):

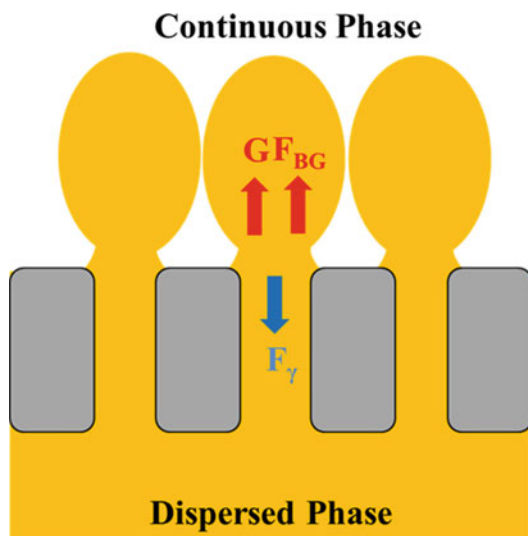
- The interfacial tension (or capillary) force (F_γ) (retaining force) that represents the effect of the

dispersed phase adhesion on the pore opening. It is a function of the dynamic interfacial tension $\gamma(t)$. This force is typically assumed to be determined by the Young-Laplace equation with the continuous phase assumed to fully “wet” the membrane surface. Surfactant type and concentration greatly influence the adsorption kinetics of the surfactant and thus the dynamic interfacial tension between the two liquid phases. During the droplet formation process, the surfactant molecules adsorb to the newly formed oil-water interface reducing the interfacial tension and facilitating droplet formation. The transfer rate of the surfactant molecules from bulk solution to the newly formed oil-water interface is mainly determined by their diffusional transfer because of the absence of continuous-phase flow.

- The buoyancy force (F_{BG}) due to the density difference between continuous phase (ρ_c) and dispersed phase (ρ_d) and influenced by the volume of droplet (V_d). It is a detaching force which counteracts the interfacial tension force or capillary force.
- “Push-off” or “push-to-detach” force (G), that is, an additional detaching force applicable when there are a large number of drops at the membrane surface causing drops to deform from their thermodynamically more stable spherical shape. The contribution of this additional force is likely to be more noticeable with a regular array membrane, such as micro-sieve metallic membrane with highly uniform pore spacing and pore size

Static Membrane Emulsification,
Fig. 1 Static membrane emulsification





Static Membrane Emulsification, Fig. 2 Forces acting on the droplets forming at the membrane pore level in static membrane emulsification

compared to conventional membranes such as the Shirasu porous glass (SPG) type.

The dispersed phase flux has a great influence on the spontaneous droplet formation behavior and depends on the viscosities of disperse and continuous phases and flow velocity of the disperse phase through the membrane pore. The push-off force occurs when a critical injection rate is exceeded and all, or nearly all, of the membrane pores become active. In this condition, a large number of drops grow simultaneously at the membrane surface, and the drop diameter is bigger than the distance between the pores, so that the drops push each other off at the membrane surface. In the limiting case, when only relatively few pores are active and the distance between those pores is bigger than the size of the drops, the push-off force is zero and final drop size is defined only by an equilibrium of buoyancy and capillary forces (interfacial tension). At increasing injection rate, more and more pores will be activated and the push-off force becomes significant (Kosvintsev et al. 2008).

Another parameter affecting the droplet detachment from the pore openings is the shape of the pore openings: noncircular pore openings

encouraging the spontaneous detachment of droplets. During droplet formation from tortuous pores with a noncircular cross section, the distorted dispersed phase is spontaneously transformed into spherical droplets by interfacial tension at the membrane surface because of the minimization of the interfacial free energy of the system. This phenomenon has been observed with SPG membranes (Sugiura et al. 2001; Christov et al. 2002).

The static ME has several advantages over dynamic ME:

1. Simple experimental setup
2. Low energy input
3. Suitable for the production of less viscous and/or larger droplets with uniform size because droplet breakup due to the shear force caused by a cross-flow pump is avoided

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Stem Cell

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The notion of stem cells is used to identify a peculiar kind of cells characterized by the fulfillment of two fundamental hallmarks: their ability of self-renewal and their capacity to differentiate into different cell types.

In particular, the first property refers to the possibility to undergo to numerous cell divisions without losing their stemness. This characteristic allows the preservation of the stem cell population and can be achieved through two different kinds of division: by a symmetric division in which both daughter cells are identical to the original retaining both their stem cell characteristic and by an asymmetric division in which only one daughter cell will continue to be a stem cell while the other one starts its differentiation process.

The second property is already somehow included the first and is related to their ability to give rise to specialized cells of different lineage becoming tissue- or organ-specific cells through a process identified as differentiation.

Stem cells deriving from different sources are currently classified in two different wide groups: adult stem cells and embryonic stem cells.

Adult stem cells, also identified as somatic stem cells, are present in many mature tissues and generally play a major role in protecting the system by restoring a specific function after injury as well as in maintaining tissue homeostasis. There are different sources of adult stem cells, characterized by a restricted differentiation degree (multipotent cells) which is mainly determined by the tissue of residence. The differentiation process is regulated by intrinsic genetic signals of the specific cells and environmental feature controls. The whole set of environmental factors able to support stem cell differentiation and proliferation is indicated as the “stem cell niche,” which for each tissue represent the restricted and narrow area where the adult stem cells are located. The “niche” hypothesis was proposed and developed for the first time in the hematopoietic system in mammals in 1978 by Schofield (Li and Xie 2005; Schofield 1978).

Within the human body, there are different adult stem cell niches that define the location and the physical organization of adult stem cells in the bone marrow, skin, intestine, brain, adipose tissue, dental pulp, etc. The bone marrow represents the reference tissue district for the study of the basic knowledge of adult stem cells, and it comprises both hematopoietic and

non-hematopoietic lineage of adult stem cells. The hematopoietic stem cells (HSC) give rise to the entire set of differentiated blood cells and represent a source of primary importance for their clinical application. One of the major issues related to the success of their transplantation is their unique identification through the localization of specific surface markers that are constantly pursued and updated with immense efforts devoted to this topic (Spangrude et al. 1988; Baum et al. 1992; Yokota et al. 2012).

The non-hematopoietic stem cell compartment presents mesenchymal stem cells (MSC) that can be easily isolated from the bone marrow and can differentiate, upon induction, in different cell types of the mesodermal lineage such as osteoblasts, chondrocytes, and adipocytes. The identification of the surface marker expression for the bone marrow MSCs revealed that they are positive for CD105, CD73, and CD90 and negative hematopoietic markers CD34, CD11, and CD19 and HLA-DR (Dominici et al. 2006; Satija et al. 2009).

Although the standard site for obtaining human MSC is the bone marrow, as already mentioned, MSC like cells can be obtained from a wide range of different tissues (the skin, umbilical cord blood, blood, adipose tissue, pancreas, and liver) representing a possibility to overcome the shortage of cell availability for clinical application (Al-Nbaheen et al. 2013).

Within the adult stem cell field, a groundbreaking in neuroscience was achieved in the 1990s when studies from different research groups brought to the identification of neural stem cells (NSCs). Neural stem cells can be isolated from different areas of the nervous system giving rise to both neurons and glial cells. The identification of such cells opened the possibility of finding out not only new insights in fundamental processes in neurobiology but also to study at the molecular level the process involved in neurodegenerative disease.

Embryonic stem (ES) cells derive from early-stage embryos (called blastocysts) that are 5–7 days old. The main difference with the adult stem cells is their pluripotency, meaning that they can potentially generate all kinds of

specialized cells of the body since they can differentiate into ectodermal, endodermal, and mesodermal cell types. Human embryonic stem cells grow in tightly packed colonies keeping well-defined borders at the periphery of colonies; they are characterized by the expression of a number of cell surface markers and transcription factors including stage-specific embryonic antigen-4 (SSEA-4), SSEA-3, OCT 3/4, Nanog, and the absence of hESC-negative marker SSEA-1 (Vazin et al. 2010).

Directing hESC toward a cell-specific endodermal, ectodermal, or mesodermal differentiation provides a useful tool for regenerative medicine and for pharmaceutical applications. In the literature, several cases of successful guided cell commitment toward a lineage-specific differentiation such as hepatocytes or insulin-producing β cells or functional neurons are reported. Despite this huge potential for the development of new therapeutic strategies, the challenge still remains to understand the intricate mechanisms that guide stem cell growth, cell fate decision, tissue generation, and organogenesis. This is a major issue to be considered especially in order to overcome the potentially uncontrolled growth of hESC-derived progeny and ensure safe therapeutic application. Since the generation of embryonic stem cells involves manipulation of the preimplantation stage embryo, it also erases major ethical issues that can be overcome by the introduction of induced pluripotent stem cells.

Induced pluripotent stem cells (iPS) are stem cells generated by the genetic reprogramming of somatic cells. The iPSC technology was pioneered by Shinya Yamanaka's team in Kyoto, Japan, who showed in 2006 that the introduction of four specific genes could convert adult cells into pluripotent stem cells under ES cell culture conditions. The discovery concerned the generation of embryonic-like stem cell from skin fibroblast by introducing four transcription factors (Oct 3/4, SOX2, c-Myc) that are responsible in the maintenance of pluripotency in both early embryos and ES cells (Takahashi and Yamanaka 2006; Takahashi et al. 2007; de Lázaro et al. 2014).

Although fibroblasts are the most used source for iPS, they can be derived from a wide variety of somatic cells with diverse developmental origin. These revolutionary findings opened a new scenario for a new class of stem cell therapies based on personalized regenerative medicine in which it is possible to generate patient-derived cells, covering a broad range of different applications. Patient-derived stem cells can be used for recapitulating in vitro all the landmark features that characterize a specific disease, thus representing a reliable disease modeling opening new paths for studying the pathogenic mechanism. Besides this application, they can be used for new drug development and toxicology screening.

However, many limitations exist before it can be clinically used. The use of proto-oncogenes to reach the highest efficiency of reprogramming requires permanent integration, which may create carcinogenic conditions and genomic instability. Promising results have already achieved in pre-clinical study, and new clinical challenges will be faced soon in Japan where the first human clinical study will start in 2014.

Several studies are currently ongoing in order to explore new promising alternative in iPS cell technology with the common aim of achieving new insight and promising results in tissue regeneration, most of them well summarized in a recent review of de Lázaro et al. (2014).

In the field of stem cell manufacturing practices, the introduction and realization of engineered biomaterials are promising as able to direct and promote stem cell fate decision. In this context an important role is played by the intrinsic characteristics of the material in terms of stiffness, nanostructure, degradability, and ability to promote cell adhesion and growth as well as chemical and physical properties. The ideal biomaterial for stem cell application has to provide a dynamic microenvironment that resembles as much as possible the physiological niche. In this way, cells can sense the material properties that trigger specific signals that dictate their fate accordingly (Murphy et al. 2014). Among the biomaterials applied for stem cell technology, polymeric semipermeable membranes are really encouraging. They provide the right support and lead the achievement of the

appropriate bio-interaction of desired cell responses which lead to a specific cell commitment. Besides their characteristics of selective transport properties and biocompatibility, they can be mass produced and easily sterilized. This determines a significant cut in terms of costs of the bioprocess related to stem cell applications. Noteworthy membrane surfaces can be tailored in a specific way allowing to mimic the features of the *in vivo* niche of a particular tissue district, thus stimulating specific cell responses. Taking into account these considerations, it is clear how a proper combination of stem cells and semipermeable membrane has a wide range of application in the field of stem cells, being a useful device for directing stem cells to differentiate in a specific cell type. Recent studies demonstrated the good interaction between stem cells and nanostructured biomaterials with a consequent enhancement in terms of new bone osteogenesis (Wang et al. 2014). Another example of the recreation of an osteoinductive microenvironment is provided by the use of a composite membrane scaffold made up of polycaprolactone (PCL) with hydroxyapatite (HA) that was used to successfully differentiate human mesenchymal stem cells in osteoblasts (Morelli et al. 2013). The ability of semipermeable membranes to provide the right physical and chemical signals to stem cell commitment was evidenced by using a chitosan membrane for the expansion and differentiation of progenitor liver cells toward adult hepatocytes. The chitosan membrane provided an optimal microenvironment in which the differentiation took place as demonstrated by the acquisition of parenchymal cell morphology, proper of fully differentiated hepatocytes, as well as by the ability to perform differentiated functions (Piscioneri et al. 2011). Within a membrane system, it is possible to recreate well-controlled and defined surroundings, and thus they can be used as *in vitro* platform to study both signaling pathways involved in cell fate specification and to highlight their action on damaged cells of different tissue districts (Piscioneri et al. 2015). In this section just a few examples of use of the membranes for stem cell applications are provided, but their tunable characteristics allow their employment in a wide range of applications.

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Stimuli Responsive

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Stimuli responsive: Stimuli responsive is a phenomenon in which materials are capable of reversibly altering their properties depending on the environmental conditions or external stimuli. External stimuli typically encompass physical (e.g., temperature, photo, redox signal, or magnetic field), chemical (e.g., pH, ionic strength, or a specific molecule), or biological (e.g., viruses or bacteria) stimuli. The stimuli-responsive membrane often involves the conformational variation of sensitive units covering on the membrane surface or the pore surface, which causes the changes in physicochemical properties, pore size, and permeation flux. The stimuli-responsive membranes are playing an increasingly important part in a diverse range of applications, such as drug delivery, diagnostics, tissue engineering, biosensors, and chemical and biological separations.

Thermo-responsive membranes can adapt to environmental temperature change due to the

thermo-responsive polymer, whose temperature-dependant solubility can reversibly solubilize upon changes in temperature and lead to conformational changes: stimulated collapse by dehydration and expansion by rehydration (Lee et al. 2010). The polymers are soluble in aqueous solution below lower critical solution temperature (LCST) through hydrogen bonding with water molecules but become dehydrated and insoluble when heated above the LCST. The typical thermo-responsive linear polymers such as poly (N-isopropylacrylamide) (PNIPAAm) exhibit sharp phase transitions around 32 °C, below which the mixture of polymer and solution is miscible. The thermo-responsive membranes prepared through grafting of PNIPAAm are often utilized for drug delivery because the LCST of PNIPAAm is close to body temperature. Usually, a significant increase of permeation flux and a reduction of rejection can be observed when the temperature increases above the LCST.

The pH-responsive membranes are prepared by ionizable polymers with a pK_a between 3 and 10. Weak acids and bases like carboxylic acids, phosphoric acid, and amines exhibiting a change in the ionization state upon variation of the pH of aqueous solutions are the candidates for preparing pH-sensitive membranes. Classical monomers includes acrylic acid (AAc), methacrylic acid (MAAc), maleic anhydride (MA), and N,N-dimethylaminoethyl methacrylate (DMAEMA). The unique properties of pH-responsive polymers arise from the facile pH adjustment which induces the ionic interaction and hydrogen bonding, resulting in a reversible micro phase separation or self-organization phenomenon (Wischerhoff et al. 2010). Thus, pH-responsive polymeric systems provide the possibility for the preparation of smart functional materials which can be used for potential therapeutic applications, e.g., controlled drug delivery based on pH-triggered release. Usually, the membranes with negatively charged surface possess a higher flux at the pH lower than the pK_a of monomer than that of at the pH higher than the pK_a .

Photo-responsive membranes usually possess photo-responsive units such as azobenzene,

spiropyran, and diarylethenes in the polymer side chains, which are capable of isomerization. Structure changes in the photo-sensitive units on membrane surface lead to changes in the macroscopic properties including wettability, charge, and mass transport.

Salt-responsive membranes can adapt to environmental salt concentration (ionic strength) and are often prepared using zwitterionic polymers of polyelectrolyte. The addition of salt was found to screen the electrostatic interaction within the polyelectrolyte, resulting in conformation changes from stretched to collapsed form (Wandera et al. 2011). Usually, the porous membrane possesses higher permeation flux and low rejection under high ionic strength due to the collapse of polymer chains and the fully open pores.

Multi-responsive membranes are responsive to more than one stimulus. Membranes exhibit responses to different stimuli such as temperature, pH, and photo that are prepared based on temperature-responsive NIPAAm and pH- and photo-responsive spirobenzopyran. Membranes fabricated by using acrylic acid, NIPAAm, and cinnamoyloxyethyl acrylate exhibit four kinds of responses to pH, temperature, ionic strength, and photo stimuli.

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Stimuli-Responsive Membranes

► Magnetically Responsive Membranes

Strip Dispersion Supported Liquid Membrane

Pietro Argurio

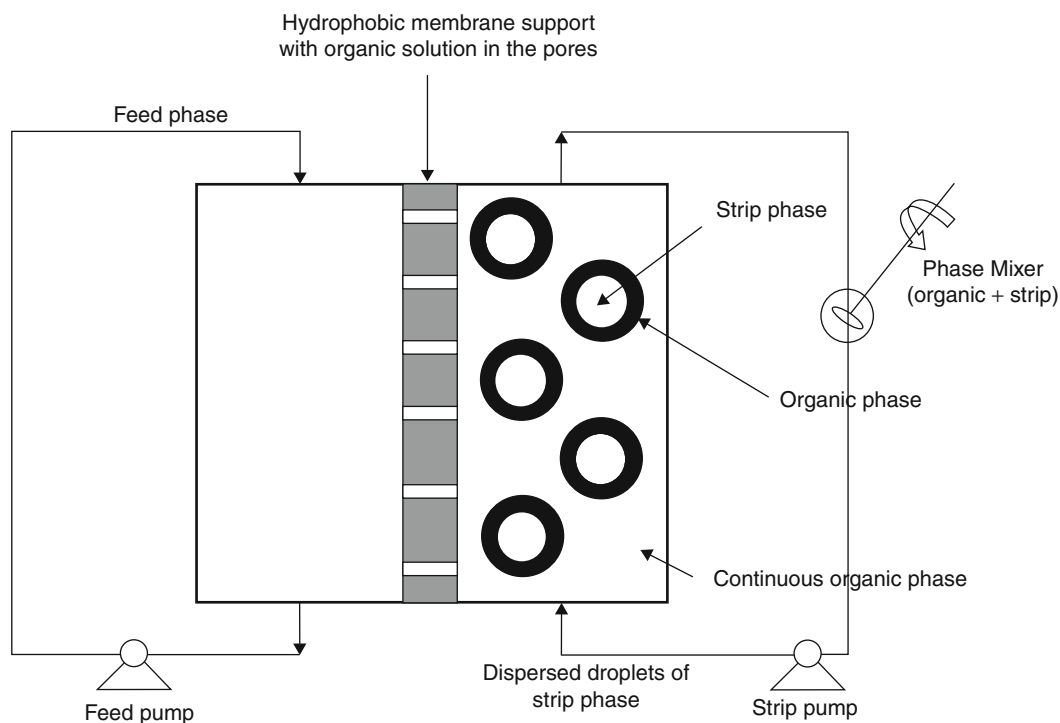
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A liquid membrane (LM) is a thin liquid film that separates two other liquid phases with which it is immiscible. There are three basic forms of LM processes: bulk liquid membrane (BLM), emulsion liquid membrane (ELM), and supported liquid membrane (SLM) (Molinari and Argurio 2009). The small membrane surface area per unit volume represents the most important drawback of BLMs, making them not attractive by a technological point of view. ELMs are characterized by a large surface area per unit source phase volume, which enhances the transport rate. One disadvantage of ELMs is the low emulsion stability, so that if for any reason the membrane does not remain intact during operation, the separation achieved to that point is destroyed. SLMs usually consist of an organic solvent impregnated in the pores of a hydrophobic microfiltration membrane (Molinari and Argurio 2011). SLM combines extraction and stripping processes into one single step, which provides the maximum driving force for the separation of a target species. SLM has many advantages over traditional separation technologies such as solvent extraction including high selectivity, low carrier and solvent consumption, high degree of concentration enrichment, and so on. Despite the abovementioned advantages, SLMs are not currently used on a large scale in the industry, since membrane stability or lifetime is, in general, far too low to assure good commercial applications. Instability of SLMs is due to the loss of carrier and/or membrane solvent from the membrane phase which has an influence on both flux and selectivity of the membrane (Kemperman et al. 1996). In addition, the flux of solute through SLM is lower because of the higher resistance of mass transfer from the presence of static membrane solution filled in microporous supports.

For solving the above difficulties and obtaining LM system with high efficiency, new configurations have been proposed. Ho (2002) and Teramoto et al. (2000) proposed a combined SLM/strip dispersion process (i.e., the strip solution was dispersed in the membrane organic phase) for the removal and recovery of target species from a feed solution. This new LM configuration has several advantages: (i) increased stability, (ii) reduced costs, (iii) increased simplicity of operation, (iv) extremely efficient stripping of the target species from the organic phase, and (v) high flux and a high concentration of the recovered target species in the aqueous strip solution. An important limitation of SLM with strip dispersion system is represented by impossibility to avoid the pollution of the aqueous solutions with membrane solution due to its dissolution in both aqueous feed and strip solutions. In this context, the choice of membrane solution with water-insoluble components is a key step.

The combined SLM/strip dispersion system can be schematized as reported in Fig. 1: a microporous hydrophobic support (e.g., polypropylene) acts as the liquid membrane support. The strip dispersion is a mixture of an aqueous strip phase, containing a stripping agent, and an organic phase containing an extractant. During the extraction process, the dispersion flows through one side of the SLM. A feed solution containing the target species is passed on the other side of the SLM.

In 2006, He et al. studied the recovery of Zn (II) ions by using the SLM/strip dispersion system. The influence of various experimental parameters on the separation of binary Zn (II) and Cu(II) ions, that is, system of great importance to hydrometallurgy and environmental protection, was investigated. Obtained results evidenced that this new configuration of LM is applicable in the separation and recovery of solutes from aqueous solutions.



Strip Dispersion Supported Liquid Membrane, Fig. 1 Schematization of the combined supported liquid membrane/strip dispersion system (elaborated from He et al. (2006))

The same LM configuration, called strip dispersion hybrid liquid membrane (SDHLM), was studied by Gu et al. (2006) for the transport and separation of Cd(II) from Zn(II) ions from aqueous media. The results evidenced that cadmium (II) can be effectively transported into the stripping solution from the feed phase by the SDHLM using tri-*n*-octylamine-secondary octanol in kerosene as carrier. The proposed system has superiority over SLMs and ELMs in terms of: (i) transport rate, since the efficient contact area between organic and stripping solution results in an extra mass transfer surface; (ii) permeability coefficient and extraction or recovery percentage of Cd(II); (iii) efficiency of uphill transport; (iv) membrane stability; and (v) no usage of high active surfactant and demulsification device.

A hollow fiber supported liquid membrane (HFSLM) with strip dispersion was tested by Li et al. (2009) in the recovery of fumaric acid from aqueous effluents. Under the optimum operating conditions, the extraction of fumaric acid was 89.5 %, and the total TOC removal reached 96.5 %. Compared with the results obtained with SLM, the extraction was enhanced by 26.6 % and the TOC removal by 9.5 %. Besides, no significant loss of the membrane phase was observed, and the stability of the HFSLM with strip dispersion system was remarkably good. A not negligible pollution of the aqueous solutions with membrane solutions was observed, so that the author concluded that further research needs to be carried out to solve this important issue.

More recently (Vilt and Ho 2009, 2011), SLM with strip dispersion has been applied to the recovery of cephalixin, an important and widely used semisynthetic antibiotic traditionally produced by a ten-step chemical synthesis. An enzymatic synthesis for cephalixin, offering several advantages over the classical route, has been developed, but it requires an in situ extraction which ensures enzyme stability. Obtained results evidenced that yield of cephalixin was increased from 32 % to 42 % when in situ removal was conducted using two hollow fiber modules and an organic membrane solution containing 10 wt. % Aliquat 336. Enzyme stability experiments showed that the organic membrane solution did

not significantly deactivate the enzyme. The final recovery of cephalixin from aqueous stripping solutions was achieved using complexing agents.

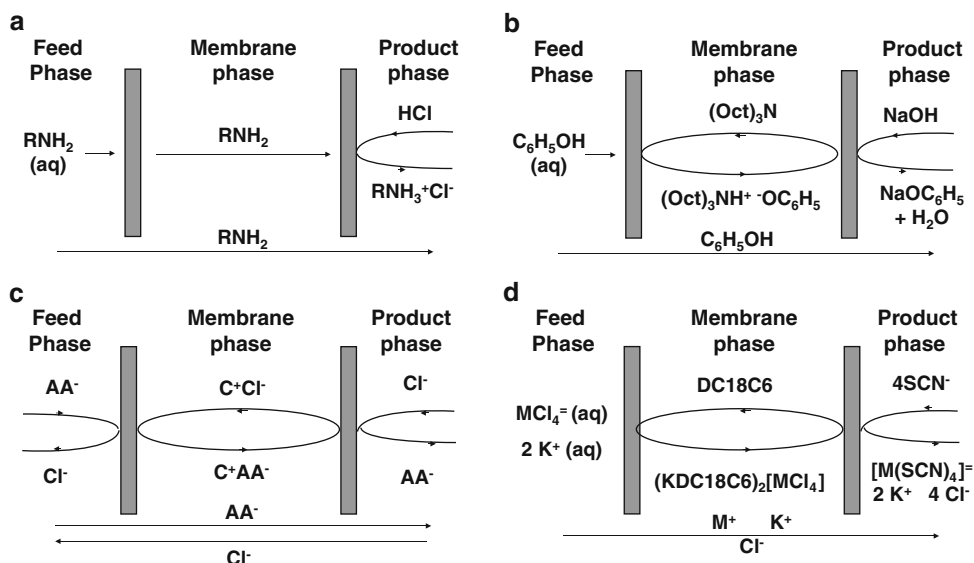
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Stripping Agents: Use in Liquid Membrane System

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Stripping agent is used in a liquid membrane system. A stripping agent is a chemical specie



Stripping Agents: Use in Liquid Membrane System, Fig. 1 Stripping agents and transport processes: (a) HCl, type 1-facilitated transport of amines; (b) NaOH, carrier-

facilitated transport of phenols; (c) Cl^- , carrier-facilitated countertransport of amino acids; (d) SCN^- , carrier-facilitated cotransport of metallic ions

which is added to the product phase of a liquid membrane to react, in the membrane/product interface, with the target species or with the complex target species carrier, giving a membrane insoluble product or simply releasing the target species in the product phase. In order to improve the effectiveness of the liquid membrane separation processes, by maximizing both the extraction velocity (flux through the membrane phase) and the reception capacity of the diffusing species in the product phase, a stripping agent is added to the product phase. This agent quantitatively reacts, in the membrane phase/product phase interface, either directly with the diffusing species to yield a membrane insoluble product, preventing it from diffusing back through the membrane (facilitated transport type 1), or with the complex formed between the target species and a carrier (added to the membrane phase to transport that target species across the membrane from the feed to the product phase), breaking that complex, removing the target species from that complex, releasing it in the product phase, in its original form or combined with the stripping agent, and regenerating the carrier, which initiates a new transportation cycle (facilitated transport type 2) (Vitt et al. 2010).

When the reaction between the diffusing species and stripping agent leads to a membrane insoluble product, the concentration of that diffusing species is reduced to zero on the product phase, resulting in high concentration gradient across the membrane phase and, consequently, in a high driving force for the transport of the target species. When the reaction between the stripping agent and the target species-carrier releases the target species in its original form, the driving force for the transport of the target species is maintained by a concentration gradient of a second species transported in the opposite direction. The selectivity of the process can also be further enhanced by the proper choice of the stripping agent in the product phase. Figure 1 shows different stripping agents used in different membrane separation processes.

The nature and concentration of the stripping agent has an important effect on the effectiveness of the transport process (Chakraborty et al. 2010). Many chemical compounds can be used as stripping agents; their choice should be determined by the nature of the target species to be removed and recovered and by the nature of the carrier, if carrier-mediated transport is used. Though acids and bases are among the more widely used

stripping agents, many other chemical species have also been employed in the transport of many compounds by liquid membranes. A stripping agent should include the following characteristics (Gu et al. 1992):

Soluble in the product phase but insoluble in the membrane phase

If facilitation type 1, quick and quantitative reaction with the target specie in the membrane phase/product phase interface, producing the insoluble compound in the membrane phase

If carrier-mediated transport, quick and quantitative reaction and removal of the target specie from its complex with the carrier, to release the target specie in the product phase or to form the insoluble compound in the membrane phase and, in both cases, to regenerate the carrier

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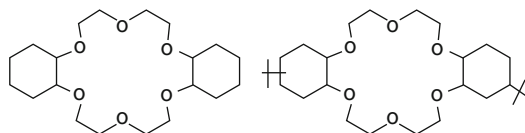
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Strontium: Removal and Recovery by Supported Liquid Membranes

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Sr-90 is one of the major heat-emitting hazardous radioactive elements present in the nuclear waste which, if separated, can not only minimize the damages to the vitrified waste blocks but also can



Strontium: Removal and Recovery by Supported Liquid Membranes, Fig. 1 Structural formula of DCH18C6 and DTBuCH18C6

have many applications as power source (Schulz and Bray 1987). Membrane-based separation methods have been tested for Sr-90 recovery from radioactive wastes which largely include UF membranes (Juang et al. 2003). This method resulted in high DF values when a Sr(II) selective sorbent (such as TiO_2) in colloidal form has been used along with the filtration step (Fabiani et al. 1986). There are also reports on electrodialysis method for Sr separation (Gasser and Nowier 2004). Liquid membrane methods such as supported liquid membrane (SLM) and polymer inclusion membrane (PIM) containing a Sr (II) selective carrier such as a crown ether have been extensively investigated by different researcher groups which showed selective Sr(II) transport (Dozol et al. 1993; Mohapatra et al. 2004). Crown ethers, such as dicyclohexano-18-crown-6 (DCH18C6) and 4,4'-(5')di-tert-butyl-dicyclohexano-18-crown-6 (DTBuCH18C6, Fig. 1), have been extensively used for the selective Sr(II) transport with the later ligand being significantly more efficient due to a lesser tendency for aggregate formation (Horwitz et al. 1990). There are reports on the transport of Sr(II) using other carrier extractants such as Cyanex 272 though the transport efficiency was very poor (Kozłowski et al. 2006).

Sr(II) recovery using crown ethers from weakly acidic feeds have used bulky counter anions like picric acid or dinonylnaphthalene-sulfonic acid (DNNS) which showed transport rates for the alkali metal ions as $\text{Ba}^{2+} > \text{Sr}^{2+} \gg \text{Ca}^{2+}$. The relative extraction efficiency of Ba(II) and Sr(II) showed a reversal when the carrier solvent contained DCH18C6 or DTBuCH18C6 in 1-octanol which suggested change in the metal ion extraction mechanism at the feed-membrane interface. However, Sr recovery

Strontium: Removal and Recovery by Supported Liquid Membranes, Table 1 Sr(II) SLM transport data from acidic feeds using crown ether-based solvents

Feed composition	Membrane configuration	Solvent system	% Sr transport (24 h)	Ref.
Nuclear fuel reprocessing concentrate	Flat sheet SLM	DC18C6 in n-hexylbenzene + iso-tridecanol (modifier)	80 %	(Dozol et al. 1993)
Synthetic nuclear waste containing 1 M HNO ₃ and 2 M Al(NO ₃) ₃	Flat sheet SLM	DTBCH18C6 in 1-Octanol	65 %	(Rawat et al. 2006)
3 M HNO ₃	Flat sheet SLM	DTBCH18C6 in 1-octanol + toluene (modifier)	~50 %	(Raut et al. 2009)
3 M HNO ₃	Flat sheet SLM	DTBCH18C6 in 80 % NPOE + 20 % n-dodecane	>98 %	(Raut et al. 2012)
Synthetic high-level waste	Hollow fiber SLM	DTBCH18C6 in 80 % NPOE + 20 % n-dodecane	>94 %	(Kandwal et al. 2012)

studies from acidic feeds using 1-octanol or analogous diluents have shown nonquantitative Sr (II) transport due to a competing acid cotransport process. Though the ionic size of H⁺ ion is much smaller as compared to the cavity size of the crown ether, it is the hydronium ion which is responsible for the competitive complexation and transport of acid. The nature of the aqueous feed with lower nitric acid concentration and higher nitrate salts have been the key to a far improved Sr transport (Table 1). The nature of the diluent also found to play a significant role in Sr(II) transport by suppressing nitric acid cotransport. Use of diluent mixtures for lower acid co-extraction was successfully demonstrated in solvent extraction studies. On the other hand, supported liquid membrane transport studies showed rapid Sr(II) transport with a much lower acid cotransport initially, though the trend showed a reversal subsequently with significantly slowed down Sr(II) transport rates and even a back transport from the receiver to the feed compartment with a resultant transport efficiency of little over 50 % (Raut et al. 2009). On the other hand, a 2-nitrophenyloctyl ether (NPOE)-based solvent containing DTBuCH18C6 has been found to be highly efficient for the quantitative Sr(II) transport even at feed acid concentration as high as 3–4 M HNO₃. The flat sheet-supported liquid membrane system containing the crown ether – NPOE solvent – showed near quantitative transport of Sr(II) which has led to subsequent development of a hollow fiber-based SLM system for >95 % Sr

(II) transport from a synthetic radioactive waste feed solution (Kandwal et al. 2012).

PIMs containing crown ethers (Mohapatra et al. 2004) and calixarenes (bis-amide or bisester containing calix[4]arenes) have been found to be quite effective for Sr(II) recovery from acidic feeds, and dinonylnaphthalenesulfonic acid (DNNS) was found to positively influence Sr(II) transport when used along with the calixarenes (Arena et al. 1998).

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Structured Membrane

► Monolithic Membranes

Structured Reactor

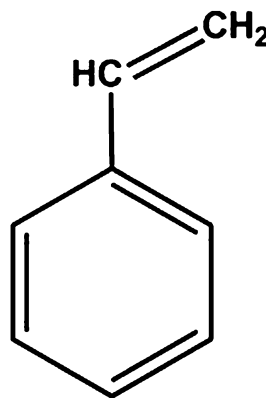
► Monolithic Reactor

Styrene-Grafted Film

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Styrene is an organic compound with the chemical formula $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$. Styrene is also known as



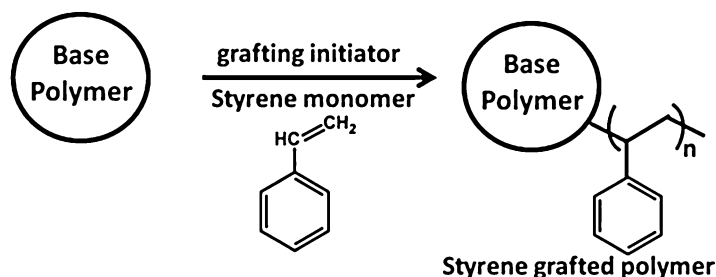
Styrene-Grafted Film, Fig. 1 Chemical structure of styrene

vinyl benzene and phenylethene. Due to the presence of vinyl group, styrene can easily be polymerized to polystyrene. Styrene can also be used as precursor for several copolymers and also can be used for graft polymerization or grafting (see graft polymerization) (Fig. 1).

Styrene is of commercial importance and used in the production of commercially significant products including polystyrene, styrene-butadiene rubber (SBR), acrylonitrile butadiene styrene (ABS), styrene-butadiene latex, styrene-isoprene-styrene (SIS), styrene-ethylene/butylene-styrene (S-EB-S), styrene-divinylbenzene (S-DVB), styrene-acrylonitrile resin (SAN), and unsaturated polyesters. These materials are used in rubber, plastic, insulation, fiberglass, pipes, automobile and boat parts, food containers, and carpet backing.

The presence of the vinyl group allows styrene to graft onto base polymer matrix. Styrene-grafted films could be produced by grafting onto ready-made polymer films, or films can also be prepared after grafting process depending upon the nature of base polymer and the degree of grafting (Sherazi et al. 2008; Hwang et al. 2015). Another advantage to graft styrene monomers is that it contains benzene ring which is readily amenable to some application based functionalization such as sulfonation, halomethylation, (Gubler et al. 2005; Varcoe and Slade 2005) etc.

Many of the polymers have been investigated for the grafting of styrene and followed by

Styrene-Grafted Film,**Scheme 1** Styrene grafting onto polymer

sulfonation to develop membranes for fuel cells applications. Almost all commercially available fluorinated polymers, such as polytetrafluoroethylene (PTFE) (Ismail et al. 2005), Teflon-FEP (Saneto et al. 2005), fluorinated ethylene propylene copolymer (FEP) (Nasef et al. 2000), tetrafluoroethylene perfluoro(propyl vinyl ether) copolymer (PFA) (Cardona et al. 2002), polyvinylidene fluoride (PVDF) (Elomaa et al. 2000), ethylene-tetrafluoroethylene copolymer (ETFE) (Scott et al. 2000), polychlorotrifluoroethylene (PCTFE) (Zhao and Jin 1988), etc., were reported to be used for grafting with styrene. Styrene-grafted films have also been developed using polyethylene (Sherazi et al. 2008, 2009, 2013) as base polymer. Styrene-grafted and sulfonated poly(ethylene terephthalate) films were also studied as bioactive polymers to produce a “biointegrable” artificial anterior cruciate ligament (ACL) (Ciobanu et al. 2006). The scheme of styrene grafting onto polymer to produce styrene-grafted film can be represented by Scheme 1.

Grafting can be initiated by various methods including chemical initiator, radiation technique, etc. (see graft polymerization).

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Submerged Biocatalytic Membrane

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Submerged membrane bioreactor (SMBR) systems have mostly been used to treat industrial wastewater, domestic wastewater, and specific municipal wastewater, where stringent discharge standards were required in order to make it usable. It is expected, however, that membrane bioreactors systems will increase in capacity and broaden in application area due to future, more stringent regulations and water reuse initiatives. In the early 1990s, MBR installations were mostly constructed in external configuration, in which the membrane modules are outside the bioreactor and biomass is recirculated through a filtration loop. After the mid-1990s, with the development of SMBR system, MBR applications in municipal wastewater extended widely. The application of submerged membrane bioreactor is mainly for the waste water treatment whilst for other possible application like recovery/production of value-added component, in biotechnological application, in food processing, etc., a few examples are still known. The development of submerged biocatalytic membrane reactor (SBMR) containing the biocatalyst immobilized within the membrane for these production systems has been reported.

The enzymatic biphasic processes are of increasing use in the production, transformation, and valorization of different biomass-based raw materials. Important applications have been developed in the fields of food, drinks, fine chemicals synthesis, pharmaceutical grade products, and cosmetics or even for clean and green

environmental purposes. Most of the time, the reactions and separation of the product are carried out in a classical side stream enzymatic membrane bioreactor.

The conventional side stream enzyme membrane bioreactor (MBR) could be used as a continuous process in which enzymes are separated from end products with the help of a selective membrane layer. In two-phase bioconversions membrane acts as a support for the interface between two distinct liquid phases. The membrane not only separates the phases, but also provides interfacial contact area and, together with the enzyme, acts as an interfacial catalyst. A complete retention of the enzyme within the system is an important requirement for a successful continuous operation of membrane bioreactor with immobilized enzyme. Upon this retention, the enzyme becomes confined to a defined region of the membrane reactor, where reaction with the substrate occurs. Two compartments partitioned by enzyme-loaded membrane, promote reaction and product separations simultaneously.

The concept of the two separate phase membrane reactor has been explored using the enzyme-loaded membranes in the submerged configuration (Chakraborty et al. 2012). The submerged membrane promotes both catalytic and separation processes. The hydrolysis of triglycerides into fatty acids and glycerol has been used as a model reaction to study and optimize the submerged enzyme-loaded membrane performances. The work has been focused on the study of the enzyme immobilization within the submerged membrane module, evaluation of the performance of the submerged enzyme-loaded membrane as a function of physical chemical and fluid dynamics conditions, testing of the submerged membrane reaction system with real fried cooked oil.

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Submerged Flat-Sheet Module

► Submerged Membrane

Submerged Membrane

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Synonyms

Submerged flat-sheet module

Submerged (immersed) membrane (SM) is an original idea, representing cheaper alternative to conventional membrane modules employed in cross-flow system. SM design involves placing flat or capillary membranes directly in the tank, usually vertically (capillary can also be laid horizontally). The air (or other gas) is supplied from the bottom of the tank. Very small transmembrane pressure (below 1 bar) is generated hydrostatically but often enhanced by a small vacuum. Although the permeate flux is smaller (up to 35 LMH)

compared with the cross-flow, which requires a larger membrane surface area, but then power consumption is significantly lower. In conventional cross-flow systems, the feed flows tangentially to membrane surface to reduce the concentration polarization or to remove cake. Therefore, conventional (cross-flow) membrane system solutions consume large amounts of energy to maintain the flux, which often exceeds 10 kWh/m^3 for circulation. Moreover, in a typical membrane modules (especially capillary, spiral, and flat plates), the requirements as to the materials combined with a complicated structure cause additional serious costs. Another important parameter is the right choice of membrane material (chemical compatibility) as well as appropriate pore size distribution. Membranes should have the narrowest pore size distribution as possible. There is also a rule that the smaller the pore size, the smaller is the tendency for the inner pore blocking, which may be irreversible.

In immersed membrane systems (Fig. 1), the innovative approach is to take use of the newer concepts such as critical flux theory or turbulences generated by gas sparging. The role of gas sparging in submerged membrane is similar to cross-flow (to facilitate turbulences) but much more cheaper. The gas flowing between the capillaries or sheets causes reciprocal and gentle movement that keep the flow of permeate flux with lower amount of energy (below 3 kWh/m^3).

Submerged Membrane,

Fig. 1 Submerged membranes



In some cases the costs for periodic backflushing and/or cleaning of membranes (CIP cleaning in place) have to be added. This requires the use of additional expenditure on chemicals and to dispose and further complicates the process (automation) and causes the system downtime. However, during ultrafiltration, only stopping of the plant, is sufficient for polarizing layer that spontaneously be dissolved in the core (bulk) due to back-diffusion. In the microfiltration process, the gas sparging gently moves the membranes which cause crushing of the filter cake layer. In individual cases, where possible, it is used in addition to other methods of cleaning the membranes, such as flushing of the liquid phase (penetration) or gas phase and chemical cleaning of various intensities. Thus, the best adapted strategies for cleaning the submerged membranes should be adapted for the specific case. The chemically supported backflushing is used daily, chemical cleaning of high concentration once per week, or intensive chemical cleaning annually.

The main advantages of SM system should therefore be low investment costs, which result from a simple and reliable design, easy installation, and compact size (small footprints). Low operating costs result from the low power consumption, low maintenance costs, and ease of use and repairs, through continuous monitoring. In addition to these economic advantages, submerged membrane also features high performance and high efficiency. Submerged membranes can be easily used for retrofitting (expansion and modification) of existing systems. Thanks to its numerous advantages, submerged membranes found itself since its inauguration popularity in the following areas:

- Food industry (beverages, alcohols, dairy)
- Chemical industry
- Electronic
- Mechanics
- Laundries
- Bathing
- Photo
- Medicine
- Agriculture (livestock and aquaculture)
- Wastewater treatment

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Submerged Membrane Bioreactor

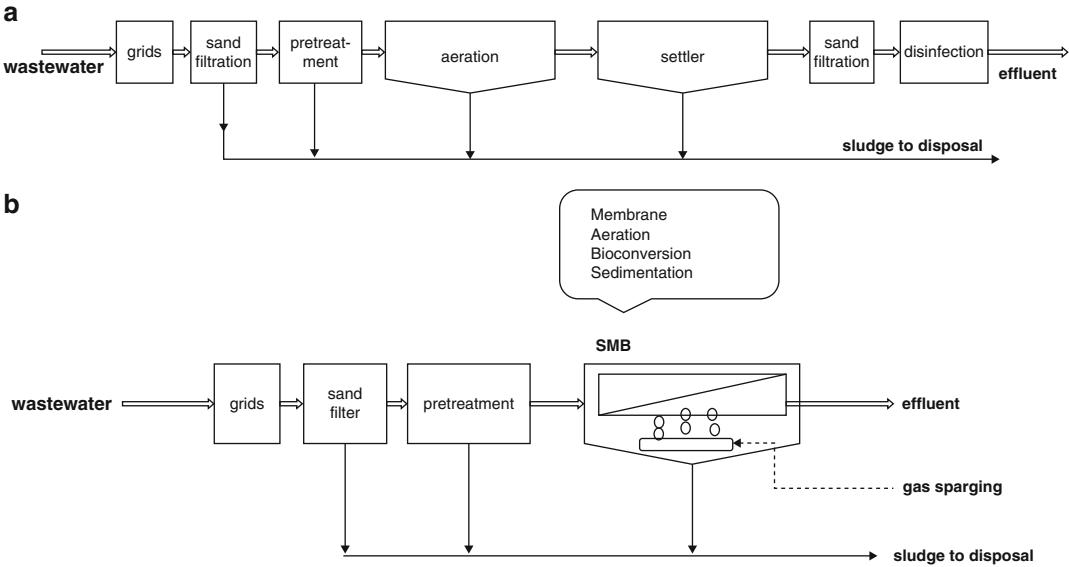
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Synonyms

Immersed Membrane Bioreactor (IMBR)

Submerged membrane bioreactors (SMBs) are a type of membrane bioreactor MBR, where two processes, i.e., the chemical reaction and separation, took place simultaneously to produce a synergistic effect. The first idea of membrane reactor connection was founded at Rensselaer Polytechnic Institute, Troy, New York (Smith et al. 1969). The first use of MBR to the activated sludge in wastewater treatment plants has been done by Dörr-Oliver, Inc., Milford, Connecticut, USA (Hardt et al. 1970). After several years this idea was popularized in Japan and developed by Yamamoto et al. (1989) and the company KUBOTA, which introduced further integration in the form of flat sheet membranes immersed directly in the reactor tank. The first application of submerged membrane reactor is the sewage system, which is considerably simplified comparing to conventional (see Fig. 1). The rapid development of SMB applications has been caused by the following: (1) legislation, (2) local water scarcity, (3) return on investments, (4) environmental impact, and (5) public and politician acceptance (Judd 2011).

Flat plate or capillary membranes are usually immersed vertically in a tank where feed is



Submerged Membrane Bioreactor, Fig. 1 Comparison between (a) conventional wastewater plant and (b) SMB wastewater plant

Submerged Membrane Bioreactor, Table 1 Comparison of two types of membrane bioreactors manufactured by ZENON[®], i.e., sidestream tubular MBR and submerged SMB (Cote and Thompson 2000)

	Membrane bioreactor MBR	Submerged membrane bioreactor SMB
Model	Permaflow Z-8	ZeeWeed ZW-500
Surface area [m ²]	2	46
Permeate flux [l/m ² h = LMH]	50–100	20–50
Pressure [bar]	4	0,2–0,5
Airflow rate [m ³ /h]	–	40
Energy [kWh/m ³]	4–12	0,3–0,6

delivered. The capillary membranes can also be arranged horizontally (see Table 1). The permeate is discharged by means of collectors on the outside of the tank under hydrostatic pressure or light vacuum using a pump. The integration of membrane and reactor introduces well-known benefits, such as accelerating the kinetics of the process and increasing its efficiency. Continuous removal of the products from the reaction space and the

retention of the substrates shifts the equilibrium to the right (toward product), thus increasing the efficiency of the process. In this case, the membrane also helps to avoid adverse reactions, which can lead to transient products. Submerged membrane bioreactors are much more cost-effective when compared to conventional cross-flow membrane modules (see Table 1).

The role of the costly cross-flow has been replaced in SMB by mild hydrodynamic conditions, where gas sparging is often used (see Fig. 2). For this purpose, the gas is supplied from the bottom so as to flow over the surface of the membrane. The role of gas sparging in submerged membrane bioreactors is twofold, i.e., hydrodynamics and mass transfer enhancement. The gas flow increases the turbulence and produces smooth movements which help to remove the filter cake from the membrane surface during microfiltration and reduces the concentration polarization layer during the ultrafiltration. In the case of aerobic bioreactor, the gas may simply be air. In the case of anaerobic bioreactors, inert gas is used to assist desorption of gaseous products from the liquid.

The SMB is most often used to remove xenobiotic and various biological nutrients, i.e., substances such as carbon, nitrogen, and phosphorus,

for the treatment of municipal, industrial wastewater, water treatment, and recycling of different process waters. SMB is also used for the purification of groundwater and surface waters (Yimaza et al. 2006), as well as waters for irrigation. Industrial sectors that use the SMB are food and beverages, where high loads of chemical oxygen demand must be reduced. Other sectors of the industrial wastewater treatment plants are in the textile, electronics, pharmaceutical, chemical,

metal finishing, automotive, petrochemical, and pulp and paper. SMB reactors are also used on offshore oil and gas platforms and on barges, ships, boats, and yachts (Table 2).

SMB has a lot of advantages compared with conventional systems, in particular activated sludge (ASB Yilmaz et al. 2006). The use of microorganisms floating freely allows for easier access to the substrate (a few microns) and thus a faster bioconversion compared with ASB (several hundred microns of flocks in activated sludge). SMB can operate effectively in all dilute solutions even below threshold values for ASB that is 0.01 kg COD/(m³ day). This is because the kinetics of bioconversion in the SMB is faster since it is limited only by chemical reaction, which is much faster compared to mass transport in the activated sludge. Thus, using SMB is cheap and easy, because it helps minimize capital and operating expenses. Low energy costs are associated with the use of energy-efficient method of removing a filter cake (in MF) or a polarizing film (in UF) from the surface of the membrane, such as gas sparging in moderate hydrodynamic conditions. Low capital cost based on a simple and very compact design, which consists of closely arranged membranes directly immersed in the tank bioreactor design with compact stacked membranes that are placed directly in the reactor. In addition, the SMB does not require settlers, thus occupying less space (footprint) in sewage treatment plants, which, in case of conventional solutions, can be very burdensome to the environment, particularly in the open air. Using SMB ensures greater bioconversion kinetics and shows better flexibility and versatility of bioconversion. SMB bioreactor has many other



Submerged Membrane Bioreactor, Fig. 2 Gas sparging around the capillary membranes in the laboratory stand

Submerged Membrane Bioreactor, Table 2 Comparison of main different SMBs (Yang et al. 2006)

Manufacturer	KUBOTA®	MITSUBISHI RAYON®	ZENON®
Membrane type	Flat sheet	Hollow fiber	Hollow fiber
Membrane pore size [mm]	0,4	0,1–0,4	0,04
Membrane material	PE (chlorinated)	PE	PVDF
Membrane configuration	Vertical	Horizontal	Vertical
Surface area in module [m ²]	0,8	105	31,6
Industrial plants	400	204	127
Municipal plants	1138	170	204

important features such as high-performance density and ease of membrane replacement and disposal of waste, ease of automation, and ease of design and scale-up. SMB systems are easy to operate and maintain, allow for remote monitoring and control, and are much easier to control by the operator. These characteristics predestine the SMB to development and retrofitting existing facilities. The global market is growing rapidly at a 20 % annual rate value that is estimated to exceed 1bln \$ in 2012 (Judd 2011).

The main suppliers of bioreactors with submerged membranes are:

1. KUBOTA[®], MICRODYN-NADIR[®], WEISE[®], TORRAY[®], KUBER[®] (flat sheet membranes)
2. ZENON[®], MITSUBISHI RAYON[®], SIEMENS-MEMCOR[®], KOCH-PURON[®], ASAHI KASEI[®], KMS KOREA LENNTECH BV[®], TRIQUA[®], TORRAY[®], COLLOIDE[®], MEMSTAR[®], ASIA GIANT[®], MOTIMO[®] (hollow fiber)
3. NORIT[®] (tubular)

Cross-References

► Aerobic Membrane Bioreactor

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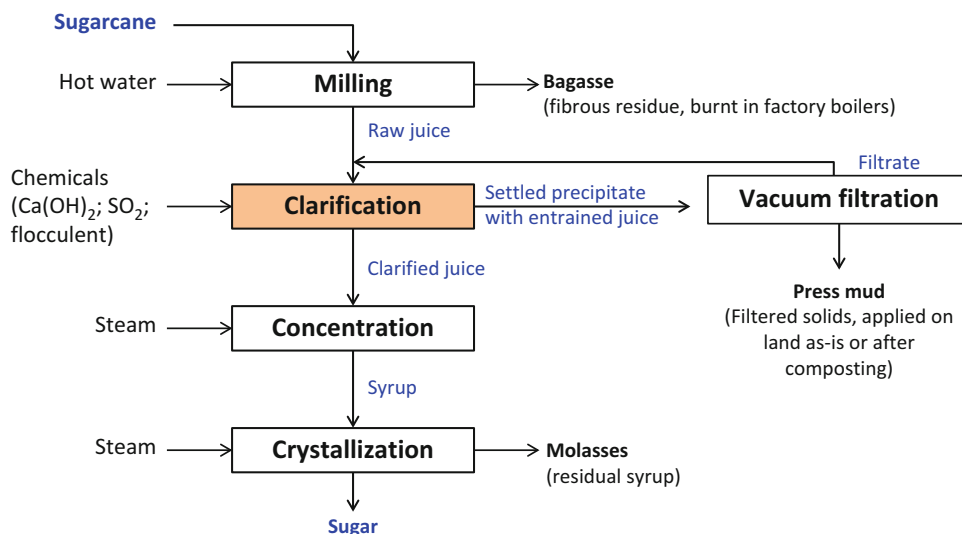
Sugarcane Juice, UF Application of

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About 80 % of the world's sugar (sucrose) production comes from sugarcane. The sugarcane is milled to extract the juice, which is then screened to remove bagasse particles, the fibrous residue from sugarcane milling. The screened juice is clarified, concentrated in multiple effect evaporators, and the syrup crystallized to obtain sugar crystals. The residual syrup (molasses) is rich in sugars and minerals; it is used as a sweetener, in cattle feed, and in production of ethanol and biochemicals. Figure 1 shows the production process.

The raw juice contains colorants and color precursors (3–5 % soluble solids), besides organic nonsugars such as proteins, polysaccharides, and waxes (0.85–1.45 % soluble solids) (Chen and Chou 1999). Ultrafiltration (UF) and microfiltration (MF) can be used for improving juice clarification (Fig. 2), which is a key step to remove nonsugar impurities. For clarification, the juice is heated to about 70 °C and treated with Ca(OH)₂ (for raw sugar) or Ca(OH)₂ and SO₂ (for “plantation white” sugar). This mixture is boiled and the precipitated impurities settled using a suitable flocculent. The clarified juice so obtained is dark brown (or brownish yellow) and somewhat hazy due to the presence of colloidal and dissolved macromolecular components; furthermore, it contains fine bagasse particles. These impurities lead to sucrose loss in molasses (thereby reducing sugar yield) and poor-quality sugar crystals.



Sugarcane Juice, UF Application of, Fig. 1 Schematic of sugar production process adapted from Ghosh and Balakrishnan, 2003)



Sugarcane Juice, UF Application of, Fig. 2 UF of clarified sugarcane juice (20kD polyethersulfone membrane; trials conducted in a sugar factory in India) (a): Retentate (b): Feed (c): Permeate

UF (or MF) of the clarified sugarcane juice enhances nonsugar removal. The filtered juice has higher purity, lower boiling times, and higher crystal growth rates. UF also reduces the calcium content in the permeate, thus controlling evaporator scaling. There are two main challenges in this application:

- Processing large volumes of hot juice in short time: even a small factory can process up to 100 m³/h of juice. High flux coupled with high concentration factors (to minimize sugar loss in the retentate) is thus essential. The clarified juice temperature is typically >90 °C. Filtration of the hot juice offers advantages of higher flux, reduced feed viscosity (making pumping easier), and minimizing microbial contamination. As sugarcane juice is prone to degradation and color formation with storage, rapid processing is required.
- Suitable membrane properties: membrane fouling (mainly due to high molecular weight polysaccharide component in the juice) is a major operational limitation. Besides, the juice composition changes considerably over the sugarcane crushing season of 6–10 months' duration. The variations originate both from

sugarcane properties (e.g., differences in varieties, soil and agroclimatic conditions, postharvest injuries to the sugarcane) and mill operation conditions (e.g., changes in milling and clarification parameters). The membrane should therefore be able to handle the variations in feed properties, be thermally and mechanically stable, and be resistant to small amounts of abrasive materials (e.g., sand) which can concentrate in the recirculation loop. It should also be easily preserved during the off-season (2–6 months, when the factory is closed for maintenance).

Both polymeric and ceramic membranes in the 3 kD to 0.2 μm range have been investigated. Ceramic membranes are more suitable with better chemical and physical stability; they can also be stored dry. Because of their higher cost, trials with ceramic membranes are limited and more demonstrations are reported with polymeric membranes. Finally, though several factory trials on UF and MF of sugarcane juice have taken place since 1990, the economic viability of the process is not established.

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Sulfonated Aromatic Polymer

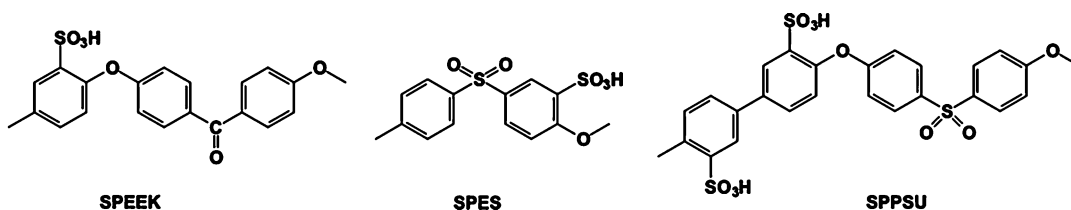
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Sulfonated aromatic polymers (SAP hereafter), as the name suggests, are polymers obtained by sulfonation of the aromatic polymers. Membranes

fabricated from the sulfonated aromatic polymers are SAP membranes. Sulfonation process imparts a number of desirable and useful properties such as high ionic conductivity, better hydrophilicity, and relatively higher solubility of the parent aromatic polymer (Vona and Knauth 2013). Sulfonation introduces sulfonic acid functionality by simple electrophilic aromatic substitution thereby enabling enhanced proton transport necessary for high proton conduction in fuel cells applications (Vona and Knauth 2013). Additionally, presence of sulfonic acid groups converts the parent polymer into ionomers without polymer chain degradation and increases its glass transition temperature (Zaidi 2003; Xing and Kerres 2006). The number of sulfonic acid groups, also called degree of sulfonation (DS in short), can be controlled by controlling the sulfonation reaction parameters, such as temperature and time (Meyer and Schrickel 2013; Zaidi 2003). A high degree of sulfonation results in swelling of the membrane which is manifested in the form of lower or reduced mechanical stability (Meyer and Schrickel 2013). Sulfonation is the best technique to make the polymer soluble in appropriate solvents especially good for thermoplastics which are not soluble in any solvents, such as polyether ether ketone. Exposing the sulfonated polymers to temperatures higher than 300 °C results in degradation of the polymer after which sulfonic acid groups are released from the polymer backbone (Meyer and Schrickel 2013; Zaidi 2003). Incorporation of sulfonic acid groups into the polymer backbone widens the scope and application of parent aromatic polymer. The applications of SAP includes such diverse and important areas as fuel cells, electrodialysis, ion-exchange resins and catalysts, surgical instruments, implant, and wound healing and dressing to name a few (Vona and Knauth 2013). SAP membranes are widely viewed by the scientific community as a possible replacement of the existing state of the art Nafion[®] membrane developed by Du Pont. Some of the key and important properties of SAP that are of interest to the scientific community and industry include ionic conductivity, water uptake, permeability, increased solubility, and mechanical stability (Vona and Knauth 2013; Zaidi 2003;



Sulfonated Aromatic Polymer, Fig. 1 Structures of common sulfonated aromatic polymers

Othman et al. 2007). Besides, SAP membranes are economical and easy to introduce sulfonic acid groups by a simple method.

Several variations of SAP based membranes such as sulfonated poly (ether ether) ketones (SPEEK), sulfonated polyphenylsulfones (SPPSU), sulfonated polyethersulfone (SPES), etc., to name a few, have been investigated as polymer electrolyte membrane in polymer fuel cells. Of these, the most studied and highly promising SAP is the polymer based on poly (ether ether ketones) or PEEK. Sulfonated PEEK (or SPEEK) is known to have high proton conductivity and high thermal and mechanical stability. High level of sulfonation makes polymer membranes amorphous and reduces its mechanical strength, making membranes brittle (Zaidi 2003; Tohidian et al. 2013). Structures of some common sulfonated aromatic polymers are shown in Fig. 1.

Sulfonation of aromatic polymer membranes can be achieved by two different approaches namely postsulfonation approach and direct sulfonation of the aromatic polymers. In this method, the aromatic polymer is first sulfonated to the desired degree and then membranes are fabricated from it. In the other approach, the membranes are first fabricated and then sulfonation is carried out on the membrane. In this case the surface of the membrane is modified, while in the other case the whole of the polymer is modified by sulfonation. However, the latter approach is most commonly used than the former for a variety of reasons. Each of the two approaches has its own advantages and disadvantages. In postsulfonation, it is difficult to control and is limited by the solubility of the polymer as it is carried out in homogeneous medium, whereas direct sulfonation consumes

large quantity of solvent and often separation of sulfonated polymer from the reaction mixtures poses a challenge. The choice of the approach is dictated by the properties and functionality desired in the SAP membranes (Vona and Knauth 2013; Meyer and Schrickel 2013; Zaidi 2003; Tohidian et al. 2013).

Sulfonation can be accomplished using a variety of sulfonating agents such as fuming sulfuric acid, concentrated sulfuric acid, chlorosulfonic acids, and sulfur trioxide (both in liquid and gaseous forms) (Vona and Knauth 2013; Meyer and Schrickel 2013; Zaidi 2003). These agents are classified as strong and mild agents and consequently affect the final yield and extent of sulfonation. As with any organic reaction, sulfonation process is also marred with unwanted side reactions, cleavage of chain to mention a few if not properly carried out especially with fuming sulfuric acid (Meyer and Schrickel 2013; Zaidi 2003). Each of these sulfonating agents has some adverse effect on the sulfonation process. Use of fuming sulfuric acid generates lots of water as a by-product thereby promoting the reverse reaction, i.e., desulfonation. The generation of HCl as a by-product limits the use of chlorosulfonic acid as a sulfonation agent as the generated acid must be neutralized. Some milder forms of sulfonating agents are trimethylsilyl chlorosulfonate, acetylsulfate, or a complex of SO_3 with amine or trialkyl phosphates also commonly used (Meyer and Schrickel 2013; Zaidi 2003). Choice of the sulfonating agent depends on the kind and type of the aromatic polymer and its molecular weight. Utmost care should be taken when sulfonation reaction is carried out to avoid these side reactions.

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Sulfonated Block Copolymer Membrane

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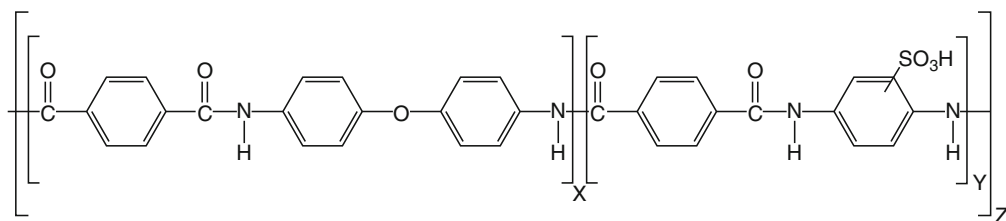
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When two different monomers couple in all possible ways, it gives rise to what is known as a copolymer. Depending on the coupling pattern, copolymers are of following three types: random copolymer, block copolymer, and graft copolymer. In block copolymer, two separate chains (or blocks) of two monomers A and B are linked together as shown in Fig. 1. A typical structure of a multiblock copolymer is shown in Fig. 2.

It is well established in literature that sulfonated polymer membranes have superior properties such as high proton conductivity, higher glass transition temperature, and higher mechanical, thermal, and chemical stability as compared to non-sulfonated or parent polymeric membranes. It is also well known that a sulfonation process introduces sulfonic group functionality which is the main reason for high performance of these sulfonated membranes. Chemical modification of polymeric materials by treatment with a variety of sulfonating agents has given birth to a host of sulfonated polymeric membranes such as sulfonated polyimides, poly(ether ether ketone)s (PEEK), poly(ether sulfone)s (PES), poly(phenylene sulfide) (PPS), etc. with improved properties. Sulfonated polymer membranes however have their own disadvantages. Sulfonation of polymers is prone to side reactions resulting in cross-linking. Additionally, due to the inherent insolubility of sulfonated polymers, the nature of the solution changes from homogenous to non-homogenous as a result of sulfonation process (Meier-Haack et al. 2005). High degree of sulfonation is essential for higher proton conductivity but it causes swelling and a consequent loss of mechanical strength (Meier-Haack et al. 2005; Yeo et al. 2012; Lee et al. 2013a). The aforementioned problems can be overcome partially if not completely by using a sulfonated block copolymer. The unique feature of sulfonated block copolymer is the existence of micro-phase separation since the two blocks are chemically different and incompatible while covalently bonded to each other. The micro-phase separation is a function of the chemical nature of the different blocks and/or length of the blocks. The presence of high density of sulfonic groups on the hydrophilic side results in a well-connected phase-separated ion transport path which enhances proton conductivity without affecting physical properties (Lee et al. 2013a). Polystyrene is an example of a block copolymer which exhibits phase-separated



Sulfonated Block Copolymer Membrane, Fig. 1 Typical coupling pattern in a block copolymer



Sulfonated Block Copolymer Membrane, Fig. 2 General structure of a typical multiblock copolymer: sulfonated poly(arylene ether amide) multiblock copolymer

morphology (Meier-Haack et al. 2005). This morphological feature of block copolymers is most desirable especially in electrochemical applications such as in direct methanol fuel cells (DMFC) and in water treatment. Many studies dealing with sulfonated multiblock copolymers with ion exchange capacities (IEC) ranging from 4.1 to 5.6 meq/g for fuel cells applications have been reported, for example, sulfonated polymer obtained from 4,4'-dichlorodiphenyl sulfone (SDCDPS), and hydroquinone shows IEC value of 4.1 meq/g. Another interesting sulfonated block copolymer obtained from 4,4'-dichlorodiphenyl sulfone and bis(hydroxyphenyl)fluorene shows IEC value of 4.5 meq/g (Takamuku and Jannasch 2012). It is also reported that sulfonated multiblock copolymer membranes have higher proton conductivity at high temperatures and low relative humidities (RHs) as compared to sulfonated polymer membranes (Meier-Haack et al. 2005; Yeo et al. 2012; Takamuku and Jannasch 2012). Sulfonated block copolymer membranes also find application in water treatment for removal of ionic pollutants from wastewater where block copolymer comprising of polystyrene sulfonate (PSS) and hydrogenated polyisoprene (hPI) has been used for membrane fabrication (Yeo et al. 2012). Reverse osmosis (RO) and nanofiltration are currently the most widely used technique for water treatment, where the use of sulfonated block copolymers has been investigated to improve the mechanical integrity and enhance water permeability. In a recent report, sulfonated block copolymer comprising of polystyrene sulfonate (PSS) and hydrogenated polyisoprene (hPI) blocks has been

employed as a nanofiltration (NF) membrane with excellent results for the removal of metal ions such as copper, cadmium, and nickel ions (Yeo et al. 2012). It is believed that (hPI) chains perform a dual role of providing flexible support matrix and induce thermodynamic incompatibility with the PSS chains. This helps in controlling the self-assembly of structures in the nanometer scale (Yeo et al. 2012). Additionally, these nanostructured membranes allow higher water flux as compared to conventional RO membranes due to sulfonated block copolymers (Lee et al. 2013b).

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Sulfonated PEEK (SPEEK)

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Sulfonated poly(ether-ether-ketone) (SPEEK) is a fluorine-free ionomer: each repeat unit consists of an aromatic backbone of 1,4-disubstituted phenyl groups separated by ether (–O–) and carbonyl (–CO–) linkages, with the –SO₃H group generally bonded to the oxy-phenylene-oxy unit (Fig. 1).

Poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene), known as PEEK, is a relatively new semicrystalline polymer, first appearing in the literature in the early 1980s (Rae et al. 2007), with high melt and glass transition temperatures ($T_m = 340\text{ }^{\circ}\text{C}$, $T_g = 143\text{ }^{\circ}\text{C}$) and melt processable. PEEK exhibits high thermal stability, toughness, and chemical and mechanical resistance.

Sulfonation of PEEK can be achieved by postsulfonation reaction or polymerization of sulfonated monomers and enhances hydrophilicity and solubility in polar solvents while providing acidity and proton conductivity.

The PEEK postsulfonation can be performed in concentrated sulfuric acid, chlorosulfonic acid, by pure or complexed SO₃, by acetyl sulfate, and methane sulfonic acid, although the low solubility of PEEK complicates the reaction. PEEK sulfonation in sulfuric acid is an electrophilic substitution reaction, in which the sulfonating agent reacts with the hydroquinone segment of the polymer chain activated by the ether linkages. The degree of sulfonation (DS), which can reach 1.0 as maximum value, can be controlled by changing the

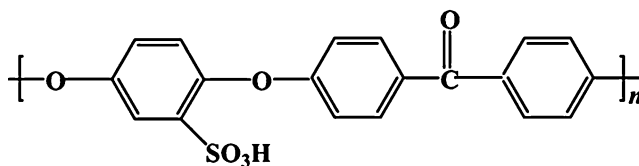
reaction time, temperature, and sulfonating agent/PEEK ratio (Fathime et al. 2007). Modified PEEKs, containing a lactonic group (PEEK-WC, WC = Cardo group), are amorphous polymers and soluble in many organic solvents so that they are more suitable for sulfonation reaction, which is carried out at room temperature and at shorter times with respect to traditional PEEK (Fontananova et al. 2010).

The direct synthesis of SPEEK offers some advantages with respect to postfunctionalization, such as: (1) a better control of the concentration and the position of the sulfonic group (e.g., *meta*-, *para*-, and *ortho*-); (2) avoiding cross-linking and other side reactions, resulting in better thermal stability and mechanical properties (Gil et al. 2004); and (3) the possibility to control the distribution of the sulfonic groups along the polymer backbone, thus obtaining block polymers.

The solubility of PEEKs in polar aprotic solvents, such as DMF, DMAc, DMSO, and NMP, offers a convenient process for the fabrication of membranes by solution casting (Xing et al. 2004). SPEEK membranes are studied as alternative to perfluorosulfonic acid membranes (PFSA) in polymer electrolyte membrane fuel cells, due to their good mechanical properties, thermal stability, and proton conductivity.

Water uptake of SPEEK membranes increases with increase of the ion exchange capacity (I.E. C. = meq of –SO₃H groups per 1 g of dry membrane) and affects mechanical properties and proton conductivity, which also depends on the presence of well-connected hydrophilic pathways for protons. In order to get the best compromise between high conductivity, limited water uptake and good mechanical properties, several approaches are possible: cross-linking of high sulfonated ionomers, block copolymers, and composite membranes (Iojoiu et al. 2005). SPEEK

Sulfonated PEEK (SPEEK), Fig. 1 Repeat unit structure of SPEEK



membranes showed also a methanol permeability lower than that of PFSA and they are promising for applications in direct methanol fuel cells (Fontananova et al. 2010).

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Sulfonated PEEK-WC (SPEEK-WC)

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The sulfonated PEEK-WC (SPEEK-WC) is the sulfonated derivative of an amorphous polyetheretherketone called PEEK-WC or poly(oxa-p-phenylene-3,3-phthalido-p-phenylene-oxa-p-phenylene-oxy-phenylene) (Zhang et al. 1987) (Fig. 1).

PEEK-WC has a lactonic group, called cardo group (WC in the polymer name means with cardo), which prevents the crystalline organization of the polymer chains; as a consequence,

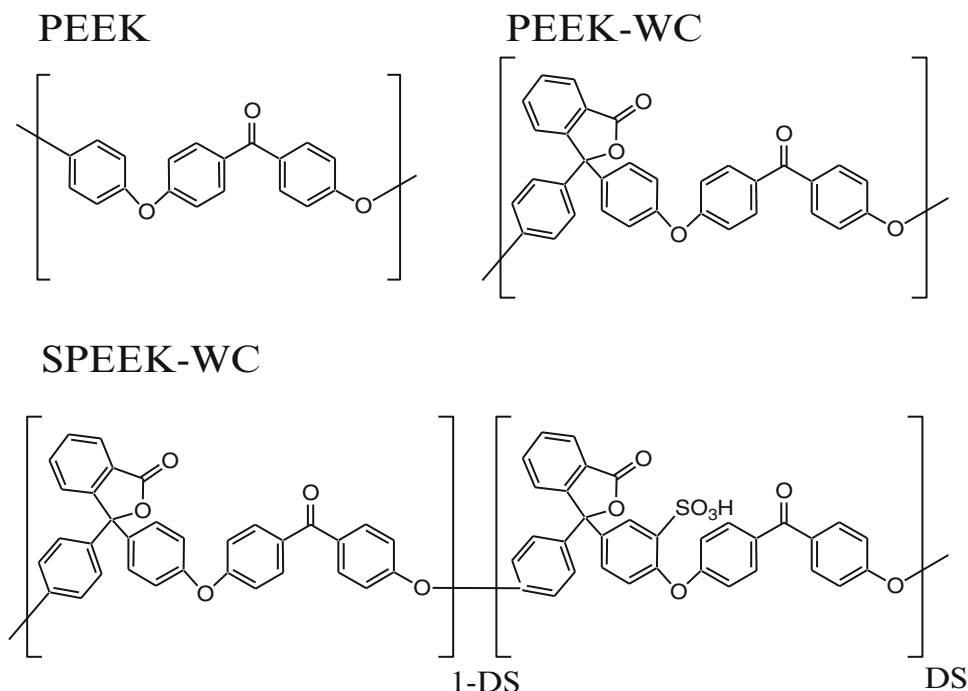
PEEK-WC is amorphous, and it is suitable for the preparation of membranes by solubilization in solvents with medium polarity (e.g., chloroform, dichloromethane, dimethyl sulfoxide, dimethylacetamide, dimethylformamide, 1-methyl-2-pyrrolidinone, etc.) and casting. On the contrary, the “classical” PEEK (Fig. 1) is semi-crystalline and insoluble in organic solvents. PEEK-WC has a high glass transition temperature ($T_g = 222\text{ }^{\circ}\text{C}$) and very good chemical, thermal, and mechanical stability.

Moreover, PEEK-WC properties can be modified by introducing specific chemical groups on the polymer chain. The reaction with chlorosulfonic acid or concentrated sulfuric acid already at room temperature introduces a sulfonic group on the aromatic ring giving a polymeric material (SPEEK-WC) with ion exchange capacity (Fig. 1) (Trotta et al. 1998). The degree of sulfonation (DS) of the SPEEK-WC can be modulated by changing the reaction time and/or temperature.

The reaction is carried out in homogenous phase and in shorter times compared to that of the traditional PEEK. For example, the reaction of PEEK with concentrated sulfuric acid at room temperature for 192 h gives a polymer with $DS = 0.85$ (Nunes et al. 2002), while for PEEK-WC the same DS can be obtained by reaction in 4 h (Drioli et al. 2004).

Sulfonated PEEK-WC is a promising non-fluorinated material for application in polymer electrolyte membrane fuel cells (PEMFCs), suitable for the preparation of membranes by casting and solvent evaporation. The sulfonation level of the polymer influences the membrane properties, in particular the ion exchange capacity and the proton conductivity, which both improve with increasing DS.

Moreover, polymeric SPEEK-WC membranes with high performance in terms of proton conductivity were recently obtained by optimizing the membrane preparation conditions (type of solvent, temperature, and post-treatment) which strongly influence the membrane microstructure and, as a consequence, the membrane transport properties and thermal behavior (Fontananova et al. 2012).



Sulfonated PEEK-WC (SPEEK-WC), Fig. 1 Repetitive unit of the PEEK, PEEK-WC, and the SPEEK-WC (DS is the degree of sulfonation)

SPEEK-WC membranes have been also modified by thermal annealing and chemical cross-linking with a diamine in order to improve their long-term durability (Fontananova et al 2013). Various ex situ characterizations were carried out on the modified and pristine SPEEK-WC membranes, including ion exchange capacity, proton conductivity, liquid water uptake, counter-elastic index, chemical resistance in oxidative conditions, and gas permeability. The results indicated that the proposed methodologies are able to increase hydrolytic and oxidative stability of the SPEEK-WC membranes.

SPEEK-WC membranes offer a higher resistance to water and methanol vapor transport than commercial Nafion membranes (which until today are the most commonly used membranes for PEMFCs). Also, the H_2 and O_2 permeabilities of the SPEEK-WC membranes are lower in comparison with Nafion (Fontananova et al. 2010).

These results justify the conclusion that less crossover problems may occur in the PEMFCs

operating with SPEEK-WC membranes compared to PEMFCs operating with Nafion.

The lower permeability of the SPEEK-WC-based membranes was due to their lower diffusion coefficients, caused by the higher stiffness of the aromatic polymer chains of SPEEK-WC with respect to Nafion.

Functional additives were also heterogenized in SPEEK-WC membranes, in order to improve their properties for applications in PEMFCs.

Mixed matrix membranes were prepared dispersing amorphous zirconium phosphate sulfophenylenephosphonate ($Zr(HPO_4)(O_3PC_6H_4SO_3H)$), in the SPEEK-WC matrix (Regina et al. 2006). The membranes obtained were characterized by a homogeneous distribution of the inorganic filler. The membranes exhibited a significantly lower swelling degree in water and methanol compared to the polymeric membranes without the filler.

Heteropoly acids (HPAs) have been also dispersed into the membrane dope solutions to

prepare mixed matrix membranes (Fontananova et al. 2010, 2012). The embedding of the inorganic HPAs, in particular the silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot n \text{H}_2\text{O}$), in SPEEK-WC membranes, enhanced the proton conductivity because the HPAs, uniformly distributed on a nanometric scale, interconnected better the ionic cluster of the polymer providing a favored pathway for protons hopping.

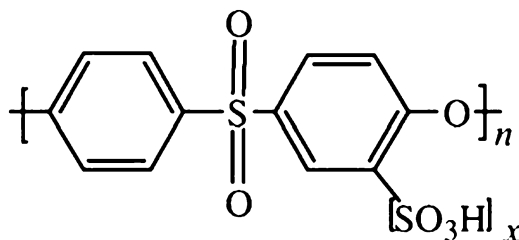
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Sulfonated PES (SPES)

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Sulfonated poly (ether sulfone) (SPES) is a sulfonic acid functionalized poly (arylene) ionomer,



Sulfonated PES (SPES), Fig. 1 Repeat unit structure of SPES

in which the aromatic rings of the polymer backbone are connected through alternate sulfone ($-\text{SO}_2-$) and (ether $-\text{O}-$) linkages (Fig. 1).

The SPES precursor, PES, is a well-known engineering thermoplastic polymer, totally devoid of aliphatic hydrocarbon groups, with a glass transition temperature of 230 °C, widely used in ultrafiltration membranes, due to its high mechanical and chemical stability (Kim et al. 1999).

The sulfonation of poly(arylene ether sulfone)s was first investigated by Noshay and Robertson in 1976, who developed a mild sulfonation procedure for the commercially available bisphenol-A-based PES (Noshay and Robeson 1976).

SPES ionomers can be prepared by post-sulfonation of PES: the reaction is an aromatic electrophilic substitution and PES is notoriously difficult to sulfonate due to the electron withdrawing effect of the sulfone linkages, which deactivate the adjacent aromatic ring (Guan et al. 2005). The sulfonic group is generally attached to the activated position ortho of the aromatic ether. The sulfonation has been carried out in heterogeneous and homogeneous media, with different sulfonating agents and solvents: $\text{SO}_3/\text{CH}_2\text{Cl}_2$, $\text{ClSO}_3\text{H}/\text{CH}_2\text{Cl}_2$, SO_3 -triethylphosphate/ CH_2Cl_2 , and oleum/concentrated H_2SO_4 . The degree of sulfonation (DS) can be controlled by changing the time, temperature, and the sulfonating agent/PES ratio. No more than one sulfonic group per repeat unit is generally substituted. By modifying the backbone structure of PES, locally and densely sulfonated PES were prepared through a selective post-sulfonation reaction on the pendant side phenyl groups along the main chains (Matsumoto et al. 2009). The sulfonation process via the metalation, such as lithiation, allowed the

introduction of sulfonate groups also in the *ortho*-sulfone site of PES (Kerres et al. 1996).

Direct polymerization of sulfonated monomers allowed the preparation of SPES copolymers exhibiting higher degree of sulfonation with respect to those obtained by post-sulfonation reaction (Wang et al. 2002; Matsumoto et al. 2009).

SPES ionomers are soluble in widely used polar solvents, such as DMF, DMAc, NMP, and at high DS they are soluble in hot water. SPES membranes can be prepared by casting organic solutions. The microstructure of SPES membranes is that typical of sulfonic acid membranes: a microphase separation between hydrophobic and hydrophilic regions occurs in the presence of water. The hydrophilic regions are responsible for water adsorption and the hydrophobic regions made up by the polymer backbone provide dimensional and mechanical stability (Dai et al. 2007). The DS affects the two phase-separated microstructures and the water adsorption, which, in turn, influences proton conductivity and mechanical properties. In order to get the best compromise between high conductivity, limited water uptake, and good mechanical properties, several approaches are possible: cross-linking of high sulfonated ionomers, block copolymers, and composite membranes (Iojoiu et al. 2005). SPES membranes showed also a methanol permeability lower than that of perfluorosulfonic acid membranes, the proton conductivity being the same, so that they are promising for applications in direct methanol fuel cells (Dai et al. 2007).

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Sulfonation Reaction

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A sulfonation reaction consists in the attachment of the $-\text{SO}_3\text{H}$ group on an organic molecule through the formation of a covalent C-S or, less frequently, an N-S bond (Kucera and Jancar 1998). Sulfonation is well known and widely used in chemical industry for many applications, such as the production of surface-active agents, detergents, ion-exchange resins, etc. Among the commercial polymers which can be sulfonated are polystyrene (PS), polyether ketone (PEK), polyether ether ketone (PEEK), polysulfone (PSU), polyphenylsulfone (PPSU), and polyphenylene sulfide (PPS) (Iojoiu et al. 2005). Sulfonated ionomers are defined as macromolecular compounds containing the $-\text{SO}_3\text{H}$ ionogenic groups. The introduction of $-\text{SO}_3\text{H}$ groups in a polymer chain provides properties such as ion-exchange capacity, hydrophilicity, solubility in polar solvents, and proton conduction

(Fathime et al. 2007). Sulfonated polymers are employed for the fabrication of membranes for fuel cells and electrodialysis, exchange resins and catalysts, surgical instruments, implants, and wound healing dressings. The sulfonation reaction can occur on the monomer before polymerization (pre-sulfonation) or on the polymer (post-sulfonation). In the case of a post-sulfonation, the degree of sulfonation depends on the type of reagent, substrate, reaction time, and temperature. This leads to a statistical distribution of the sulfonic acid groups (Kucera and Jancar 1998). The pre-sulfonation of monomers allows a better control of the degree of sulfonation, and no chemical treatment after polymerization is necessary (Gil et al. 2004).

The sulfonation reaction of aromatic rings occurs more easily than that of aliphatic compounds: the sulfur atom of a sulfonating agent is bonded to more electronegative atoms such as oxygen and acts as electrophilic center reacting with the delocalized π electron system of the aromatic ring (Kucera and Jancar 1998). The reaction can be considered a bimolecular reaction (S_E2 mechanism):

- i. A π complex between an aromatic compound (ArX) and a sulfonating agent (e.g., SO_3) is first transformed in a σ complex (rate determining step).
- ii. The sulfonated aromatic derivative is then obtained by the quick release of an X^+ species from the σ complex.

The presence of various substituents on the aromatic ring can result in the insertion of the $-SO_3H$ group in preferential positions and the formation of specific ionomers: the sulfonation of aromatic compounds bearing substituents, such as $-NR_2$, $-NHR$, $-NH_2$, $-NHCOR$, $-OH$, $-OR$, $-SH$, $-SR$, -alkyl-, -halo-, and NO , results in the prevalent formation of *para*-isomers than *ortho*-isomers; differently, in the presence of substituents such as $-R_3N^+$, $-R_2S^+$, $-NO_2$, $-CN$, $-CHO$, $-COCl$, $-SO_2R$, $-SO_3H$, $-COOR$, and $-CONH_2$, the insertion of the $-SO_3H$ group mainly occurs in the meta-position (Kucera and Jancar 1998).

The main sulfonating agents can be classified into three groups (Kucera and Jancar 1998):

1. Electrophilic reacting agents (sulfuric acid, oleum, chlorosulfonic acid, free sulfur trioxide and its complexes, trimethylsilylchlorosulfonate, etc.)
2. Nucleophilic reacting agents (sulfites and hydrogensulfites, sulfur dioxide), which react with halogen derivatives and unsaturated compounds containing multiple bonds
3. Radical reacting agents ($SOCl_2$, SO_2+Cl_2 , SO_2+O_2)

Polymer sulfonation can be carried out as a heterogeneous or a homogeneous reaction in hydrocarbons or chlorinated solvents (Kucera and Jancar 1998). As an example, the heterogeneous sulfonation of PS is very interesting especially for industrial applications. Some examples reported:

- The (solid-gaseous) heterogeneous sulfonation of PS beads of 450 nm in diameter with gaseous SO_3 above fuming sulfuric acid, for 3 days at room temperature
- The (solid-liquid) sulfonation of PS powder with 100 % H_2SO_4 in the presence of Ag_2SO_4 , preventing the formation of side products, for 5–15 min

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Sulfur Odorous Compounds Removal by Pervaporation

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Sulfur oxide emissions generated by vehicle engines may cause some serious problems, for instance, inducing the formation of acid rain, decreasing the efficiency of catalytic converters, and promoting corrosion of engine parts. As a result, removal of sulfur from gasoline has received increasing attention with growing environmental awareness. Much attention has been paid to pervaporation (PV) which is a promising and feasible technology for desulfurization of gasoline since Grace Davison Company offered the PV membrane-based S-Brane process in 2002. Mercaptans, sulfides, disulfides, thiophene, and its derivatives are the typical sulfur components of fluid catalytic cracking (FCC) gasoline in which thiophenic sulfur represented a large fraction (80 % and over) after alkali cleaning process (Lin et al. 2009). For this reason, the main aim for FCC gasoline desulphurization is to remove thiophenic sulfur compounds, at present. Unwisely, it is more difficult to remove thiophenic sulfur impurities than to other sulfur compounds in FCC gasoline.

Quite a lot of PV membranes for sulfur removal have been reported by Grace Davison Company (White et al. 2004). PUU membrane showed higher sulfur enrichment than polyimide (PI) and other commercial membranes they reported. However, its practical application is not satisfying due to the low flux (less than 0.1 kg/(m².h)). Exxon Mobil Research and Engineering Company presented two types of membrane for desulphurization which are nonionic and ionic membranes. Reported nonionic membranes included polyvinylpyrrolidone (PVP) and cellulose triacetate (CTA), while the preferred ionic membranes (Saxton et al. 2004) included Nafion RTM-type acidic membranes, e.g., Nafion

RTM117, that had been optionally treated by ion-exchange reaction or with bases. The good news is that certain investigations have been made on some commercial membranes. Marathon Oil Company also studied the process for removing sulfur from hydrocarbon, while Trans Ionics Corporation has developed a PV process, TranSep-S, for sulfur removal from gasoline boiling range feeds.

Besides, some polymer materials with sound sulfur removal performance, for instance, cross-linked polyethylene glycol/polyethersulfone (PEG/PES) composite membranes, were also used for FCC gasoline desulphurization (Lin et al. 2006). The performance of polydimethylsiloxane (PDMS) and polyimide PI membrane composite membranes was studied for sulfur removal from model gasoline (Qi et al. 2006). It has been showed that the membrane modification methods lead to achieve high selectivity or high flux (Lin et al. 2009). For example, cross-linking modification for PEG increased sulfur enrichment factor from 3.31 to 7.31 for model compounds feed and from 1 to 3.05 for FCC gasoline. AgY zeolite incorporation in PDMS membranes led to a significant increase in total flux. At the same time, higher sulfur enrichment factor and permeation flux were obtained from PEG/polyurethane (PU) blend membranes for gasoline desulphurization. It should not be ignored that the performance for various membranes mainly depends on the properties of the membrane materials while the types of membrane structure also have a significant influence on the membrane performance. Ceramic-supported PDMS membrane exhibits a higher permeation flux and an acceptable sulfur enrichment factor in comparison with those composite membranes using polymeric supports (Xu et al. 2010). The operating parameters of PV, including feed temperature, feed concentration, feed flow rate, permeate pressure, etc., have significant impacts on membrane performance. Take ceramic-supported PDMS membrane as an example; the increase of sulfur content in feed leads to a higher total flux but a lower sulfur enrichment factor. By increasing the feed temperature, the total flux increased while sulfur enrichment factor decreased. It was

appropriate that low permeate pressure and high feed flow rate were beneficial to improve total flux and sulfur enrichment factor (Xu et al. 2010).

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Supercritical CO₂ Hybrid Membrane Systems

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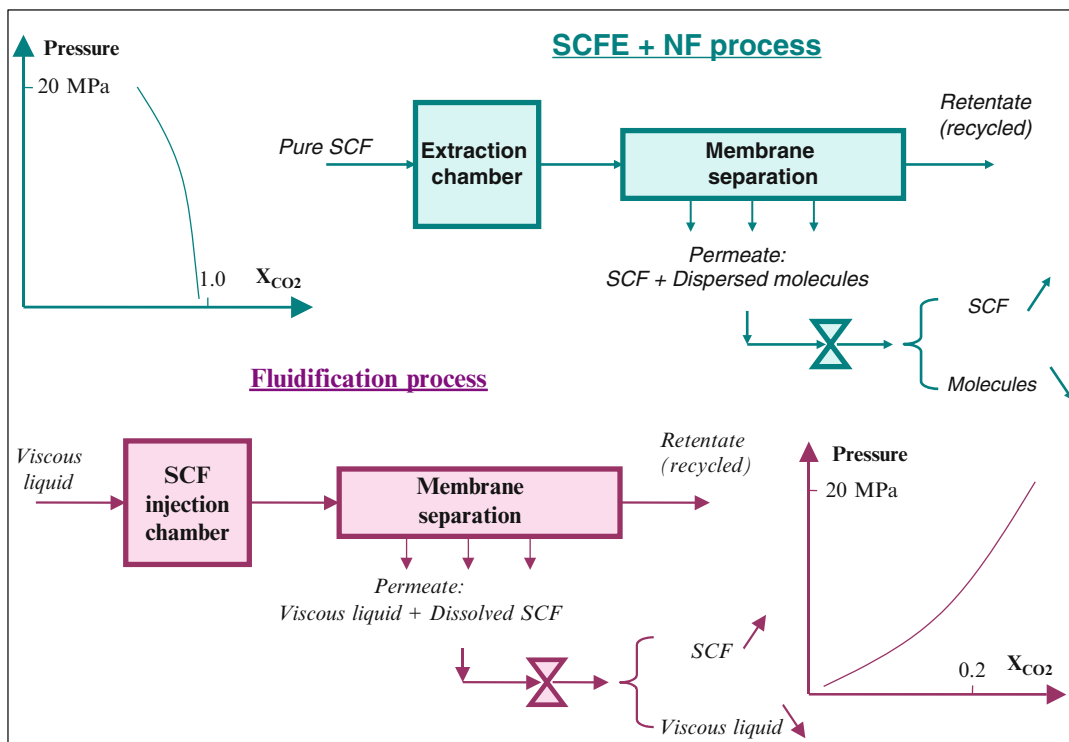
Supercritical carbon dioxide is a fluid state where CO₂ is held at or above its critical temperature (31.10 °C or 304.25 K) and critical pressure (72.9 atm or 7.39 MPa). Carbon dioxide usually behaves as a gas in air at standard temperature and pressure or as a solid called dry ice when frozen. If the temperature and pressure are both increased to be at or above the critical point for carbon dioxide, it can adopt tunable properties midway between a gas and a liquid: notably a very low viscosity (as for gas) and at the same time a very high density (as for liquids). CO₂ offers also a low toxicity and environmental impact, while the relatively low process temperature and its stability

protect most treated species from damage or denaturing. Thus, supercritical CO₂ has become an important commercial and industrial solvent particularly for chemical extraction (for decaffeinating as an example), for dry cleaning (much more attractive than hydrocarbons or perchloroethylene), for separation (by simple pressure release and control of solubility, it is possible to separate different fractions), or to produce micro- and nanoscale particles.

The use of SCCO₂ with porous barriers (MF, UF, NF) can lead to the development of new original or intensified hybrid processes. Basic ideas are summarized on the Fig. 1 above.

The part of the diagram which corresponds to high mass fraction of solvent (green on the left) may be associated to new continuous and compact processes of extraction/separation. In a first vessel, SCCO₂ extraction is carried out from mixed solutions; then the SC solution obtained is passed through a nanofiltration membrane where high-molecular compounds (retentate) are separated from small-molecular species (permeate). By a controlled pressure drop on the permeate side, solubility can be lowered, thus inducing the separation of small-molecular species (solid state) from pure carbon dioxide (gaseous); the stream of CO₂ may be recycled to the extraction chamber. On the other side, heavy molecules may be separated from the retentate by a controlled temperature change (solubility modification), before recycling the stream of SCCO₂ at constant pressure. Among the main advantages of the process are the following: important permeate flows may be obtained because of the low viscosity of SCCO₂ (10 times higher than for water); as compared to classical SC extraction process, a lot of energy may be saved because pressure cycles (relaxation/compression from standard to SC conditions) only apply to the small fraction of carbon dioxide corresponding to permeate; only one compression unit is necessary for extraction and separation steps. The feasibility of the concept has been demonstrated on different model and real solutions.

By working in the part of the diagram which corresponds to low mass fraction of solvent (purple on the right), an original process to enhance the fluidity of thick liquids in order to



Supercritical CO₂ Hybrid Membrane Systems, Fig. 1 Supercritical CO₂ hybrid membrane systems

facilitate their filtration in a membrane unit has been developed. Indeed, by inflating as an example sticky oils with the injection of pressurized CO₂, one can obtain a pseudo-homogeneous solution which exhibits a viscosity down to 10-time lower. Membrane filtration is much easier, and a pure liquid may be recovered after the operation on the permeate side by dropping pressure. Undoubtedly, this new process allows getting a better product quality than other ones already tested: at high temperatures or with chemical additives. In particular this new original process can be a one-stop tool for the treatment of fragile biological products. It represents a sustainable and safeguarding environment technology that does not ask for posttreatments (for energy or chemical additives).

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Superhydrophobicity

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Superhydrophobicity is a surface phenomenon that indicates a very low affinity to water, and, in turn, the surface is very difficult to be wetted. A generally accepted definition of superhydrophobicity is to have a water contact angle above



Superhydrophobicity, Fig. 1 Water droplet forms a bead on superhydrophobic surface (Image by Hsu SH and Sigmund W, University of Florida)

150° and a start-rolling angle lower than 10° at room temperature and ambient pressure. Therefore, water droplets on superhydrophobic surfaces typically form spherical beads (Fig. 1), and can be easily shaken away from the surface. For explanation on contact angle, please refer to the section of Young's Model. This extreme water repellency widely exists in a variety of natural species. Some crucial functions for these species are provided through this property, such as the reduction of surface contamination and the ability of performing underwater respiration or sustaining the impact from raindrops. More details can be found in the section of lotus effect and hairy superhydrophobic surface.

Superhydrophobic surfaces with the highest contact angles are the combination of surface chemistry and topography. The surface energy has to be low enough to reduce the adhesion between water and solid, and furthermore it has to be rough enough to lower the solid area which is in contact with water. Multiple scales of roughness, namely, hierarchical structures, with additional nanosized roughness existing on the top of a micron-sized feature, are often needed to achieve superhydrophobicity. More details can be found in the section of the Cassie-Baxter Model.

Since 2000, interest in superhydrophobicity has not only increased concerning the science behind this unique phenomenon but also concerning the design and engineering of such

superb anti-wetting surfaces. The most prominent effect of superhydrophobicity is the self-cleaning ability, where dirt can be effortlessly picked up and removed while water droplets roll off the surface. The consumption of water and energy is minimized to keep the surface smudge free. Other potential applications are also related to the field of energy conservation or environmentally friendly technologies, such as anti-biofouling, anticorrosion, drag reduction, and deicing surface.

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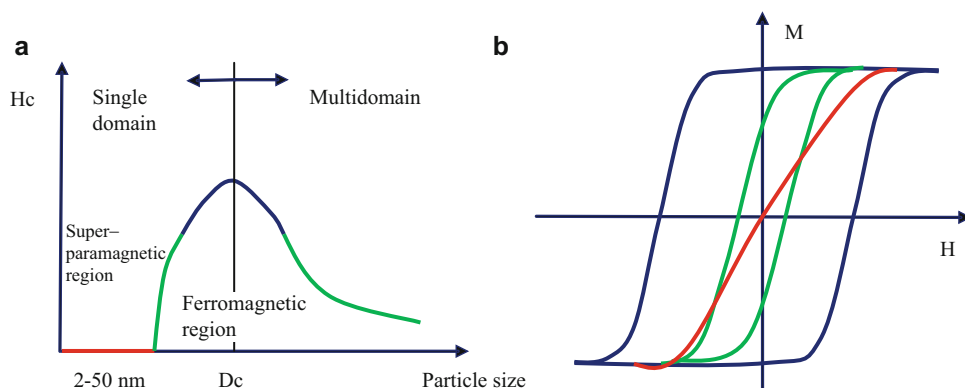
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Superparamagnetic Properties of Membranes

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Magnetic separations have for decades been essential processes in diverse industries ranging from steel production to coal desulphurization. In such settings, the magnetic fields are used in continuous flow processes as filters to enrich or remove magnetic impurities (Yavuz et al. 2009).

The interest in magneto-responsive colloidal systems and magnetic particles is steadily increasing. Both nano- and micron-sized magnetic particles have been used successfully for a wide range of applications, including treatment, diagnosis, chemical, environmental and biological separation processes. The suspensions of micron-sized magnetic particles are called magneto-rheological fluids and are preferable for some applications where the separation of magnetic microparticles from a liquid medium can be executed easily and



Superparamagnetic Properties of Membranes,

Fig. 1 Dependence of (a) a powder coercivity on the particle size and (b) a magnetization (M) on an external

magnetic field (H) for magnetic particles with various particle sizes (hysteresis loops)

economically compared with that of magnetic nanoparticles (Xu et al. 2008). Promising strategy for improving the separation properties of polymeric films is the incorporation of magnetic particles into the polymer matrix. In many cases, the polymer matrix functions as a dispersion medium which stabilizes and protects the added particles (Goyal et al. 2011). While these filler particles, incorporated in the polymer matrix, enhance membrane's mechanical, optical, magnetic or electrical properties (Zhang et al. 2006). Such procedures produce novel functionalized inorganic-organic composites, which have found extensive applications, like, for instance, in the gas separation (air) (Rybak et al. 2009a, b, 2012, 2013, 2014a, b; Grzywna et al. 2010; Krasowska et al. 2012; Borys et al. 2013; Dudek et al. 2013; Strzelewicz et al. 2013), pervaporation (Rybak et al. 2013), bioapplication, water treatment processes (Wandera et al. 2010; Yang et al. 2013; Dudek et al. 2012).

Superparamagnetic single domain nanoparticles dispersed in the liquids are called magnetic fluids, or ferrofluids. They can easily be magnetized in an external magnetic field and immediately redispersed once the magnet is removed (Tural et al. 2009). The most popular nanoparticles are iron oxide particles in two main forms, magnetite (Fe_3O_4) and its oxidized form maghemite ($\gamma\text{-Fe}_2\text{O}_3$). They have attracted extensive interest due to their superparamagnetic properties and their potential applications in many

fields, like: terabit magnetic storage devices, catalysis, sensors, and high-sensitivity biomolecular magnetic resonance imaging (MRI) for medical diagnosis and therapeutics (Papaefthymiou 2009).

Many researchers have carried out work on the application of these nanoparticles in preparation of the magnetic membranes. They have been applied in controlled release of chemicals, microreactors, biomedical, or chemical sensors, in the separation of paramagnetic and diamagnetic gaseous species at room temperature (He , N_2 , O_2 , Ar , and air separation), protein isolation, cell separation, drug delivery, biocatalysis, ion selectivity experiments, food processing, and wastewater treatment (Wandera et al. 2010; Yang et al. 2013; Dudek et al. 2012). The effectiveness of these membranes' activity depends mainly on interaction between these two materials (polymer matrix and filler), their compatibility, and good dispersion of inorganic phase. Numerous chemical modifications of polymer and inorganic phases and application of appropriate preparation techniques could be used to improve these features.

This type of membrane has the special properties because of the superparamagnetic behavior of added fillers. These particles have to be single magnetic domains with no hysteresis loops. This would be possible when their diameter will be between 2 and 50 nm (the size of nanoparticles is below a critical value D_c), depending on the used material (Fig. 1a). Another property is that

membrane's magnetization can randomly flip direction under the influence of temperature, and this typical time between two flips is called the Néel relaxation time τ_N and is given by the following Néel-Arrhenius equation:

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \quad (1)$$

where:

τ_N – the average time for the nanoparticle's random flip of magnetization due to the thermal fluctuations,
 τ_0 – the time, characteristic for the material, called the attempt time,
 K – the nanoparticle's magnetic anisotropy energy density,
 V – volume,
 k_B – the Boltzmann constant,
 T – the temperature.

They will be in the superparamagnetic state in the absence of external magnetic field, when the time used to measure the magnetization of the nanoparticles is much longer than the Néel relaxation time, and their magnetization appears to be in average zero. In this state, an external magnetic field is able to magnetize the nanoparticles, just like in the case of a paramagnet. However, their magnetic susceptibility is much larger. They have a large constant magnetic moment and behave like a giant paramagnetic atom with a fast response to applied magnetic fields (Fig. 1b) with negligible remanence (residual magnetism) and coercivity (the field required to bring the magnetization to zero).

The magnetic moments of superparamagnetic nanoparticles in an external magnetic field tend to align along the applied field, leading to a net magnetization. The magnetization curve is a reversible S-shaped increasing function. This function is quite complicated but in some cases this function may take the following forms:

- If all the particles are identical, their easy axes are all oriented parallel to the applied field and the temperature is low enough

($T_B < T \lesssim KV/(10 k_B)$), then the magnetization is given as:

$$M(H) = n\mu \tanh\left(\frac{\mu\mu_0 H}{k_B T}\right) \quad (2)$$

- If all the particles are identical and the temperature is high enough ($T \gtrsim KV/k_B$), then the magnetization is given as:

$$M(H) = n\mu L\left(\frac{\mu\mu_0 H}{k_B T}\right) \quad (3)$$

Where:

n – the density of nanoparticles in the sample,
 μ_0 – the magnetic permeability of vacuum,
 μ – is the magnetic moment of a nanoparticle,

and $L(x) = \frac{1}{\tanh(x)} - \frac{1}{x}$ is the Langevin function.

It can be seen from these equations that large nanoparticles have a larger μ and so a larger susceptibility. This explains why superparamagnetic nanoparticles have a much larger susceptibility than standard paramagnets: they behave exactly as a paramagnet with a huge magnetic moment.

Magnetic nanoparticle fillers exhibit a variety of unique magnetic phenomena that are drastically different from those of their bulk counterparts. The magnetic properties of these membranes are influenced by nanoparticles morphology, structure, size, and its distribution.

That's why the appropriate magnetic nanoparticle preparation method, which has a large effect on shape, size distribution, and surface chemistry of the particles should be selected. Such method also determines to a great extent the distribution and type of structural defects or impurities in the particles. All these factors affect magnetic behavior. The most employed method is coprecipitation in which the size and shape of the nanoparticles can be controlled by adjusting pH, ionic strength, temperature, nature of used salts, or the concentration.

The next method applies a microemulsion which is a stable isotropic dispersion of two immiscible liquids and surfactant. This dispersion consists of nanosized domains of one liquid in the other phase, stabilized by the surface-active

molecules at the phase boundary. The size of the spherical nanoparticles can be tailored and tuned by changing the size of the water pool. The third method is the decomposition of iron precursors in the presence of hot organic surfactants. It results in samples with good size control, narrow size distribution, appropriate crystallinity, and the well-dispersed nanoparticles (Cullity and Graham 2009; Dave and Gao 2009).

The development of the high-quality nanocrystals, with greater surface areas and more responsive magnetic cores, will allow an expansion of the magnetic membranes in many areas of industry, medicine, and various separation techniques.

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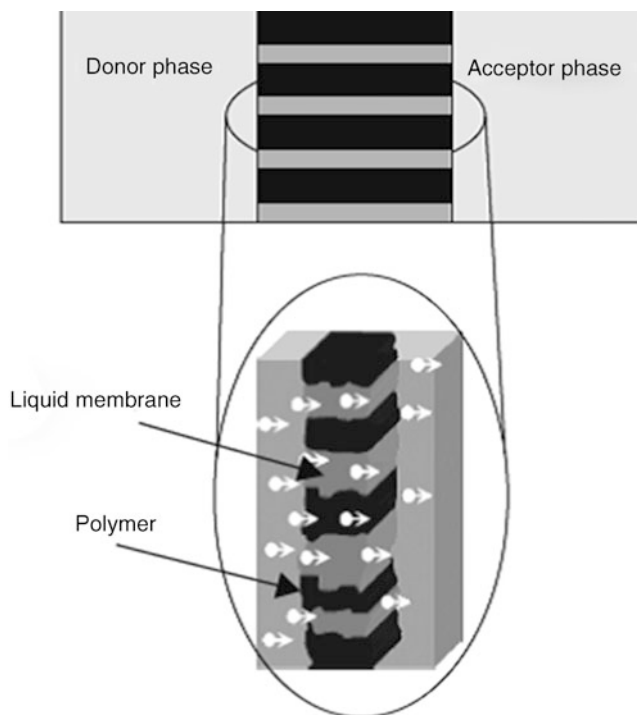
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Supported Liquid Membrane

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Supported or immobilized liquid membrane (SLM or ILM) is one of the three-phase liquid

Supported Liquid Membrane,**Fig. 1** Scheme of a supported liquid membrane

membrane systems in which the membrane phase (liquid) is held by capillary forces in the pores of microporous polymeric or inorganic film. Support separates two aqueous solutions: the feed (donor) and the strip (receiving, acceptor) phase (see Fig. 1). The compounds of interest are separated from the aqueous sample feed phase into an organic liquid membrane phase, and then they are continuously back extracted to the other side of the membrane into the strip phase. The driving force is the difference in concentration of the compounds between the phases.

A SLM usually consists of an organic solvent immobilized in the pores of a hydrophobic microfiltration membrane. In many cases, the organic solvent contains a carrier which is able to selectively bind one of the components from the separated mixture (feed solution) which improves selectivity. The general term for mass transport through liquid membranes under the chemical potential gradient as a driving force is permeation. The permeants from liquid feed (donor solution) are transported through a nonporous, polymeric, or liquid membrane phase and desorbed into

another liquid phase. Some authors called this process pertraction. While solvent extraction is an equilibrium process, SLM separation is a dynamic, nonequilibrium diffusion process governed by the kinetics of the membrane transport. Therefore, the amount of transported compounds is not proportional to the amount of the organic, membrane phase as it is in extraction.

Usually SLMs are based on hydrophobic organic solvent immobilized in a polymeric membrane separating two aqueous solutions. In some cases, the arrangements are opposite, and the pores in the support separating two nonaqueous phases are impregnated by water. The SLM may be fabricated in different geometries. Flat sheet SLM is useful for research, but the surface area to volume ratio is too low for industrial applications. Spiral-wound and hollow-fiber SLMs have much higher surface areas of the LM modules (103 and $104 \text{ m}^2/\text{m}^3$, respectively).

The main problem of SLM technology is the stability: the chemical stability of the carrier, the mechanical stability of porous support, etc. Relatively new LM technologies, developed

with the aim to improve stability parameters, are gel LM formed by liquid-phase gelation in the pores, ion-exchange membranes as supports, ionic liquids (ILs) used as a membrane phase, swollen polymeric membranes, and polymeric inclusion membranes (PIM), formed by casting the solution of polymer and plasticizer (solvent characterized by high viscosity) to form a thin, flexible, and stable film. All these technologies are considered as modifications of the SLMs. SLM can also be formed by immobilizing the membrane phase between two nonporous films which are permeable to transported substances and usually nonselective. The latter is much more stable but is less suitable due to a higher mass transfer resistance.

Successful applications of SLMs are possible due to their advantages compared to other separation methods. The main advantages of SLMs are the small amounts of organic phase and extractant (carrier) used, one-step mass transfer, the possibility of achieving high separation factors, concentration of extracted compound(s) during separation, and low separation costs. SLMs have been used to solve an increasing number of separation problems, including metal and organic compound separation and the resolution of stereoisomers. The unique flexibility and ease of preparation of SLMs in various configurations, despite some stability and lifetime problems, have resulted in their application in many sometimes very different fields where selective and efficient separation methods are necessary: in hydrometallurgy, biotechnology, wastewater treatment, the capture of greenhouse gases, analytical and environmental chemistry, and in the pharmaceutical industry.

SLM separation systems can be classified into several different groups, according to their preparation methods, types of membrane support and membrane liquids, module types used, and their application (for details, see Dzygiel and Wieczorek 2010).

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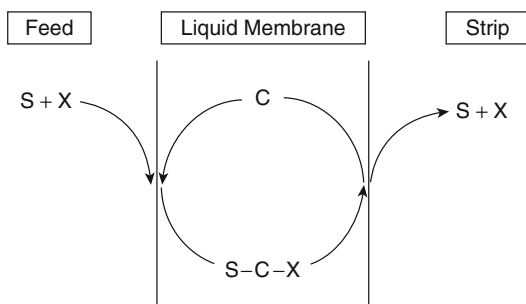
Supported Liquid Membrane for Enantioselective Separation

Keiji Sakaki

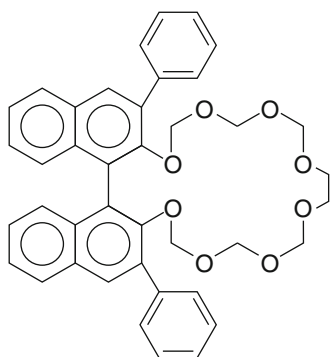
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An enantiomer is one of two stereoisomers that are mirror images of each other and nonsuperposable. This feature of an enantiomer is called “chirality.” Many chiral molecules not only appear in nature but also can be synthesized artificially. Amino acids and sugars are the representative chiral molecules found in nature, and they exist in the form of one isomer. Enantiomeric pairs frequently show different biological activity from each other. So the technology to separate enantiomers has been an important subject in the industries dealing with pharmaceuticals, foods, agrochemicals, and so on. However, enantioselective separation has been a challenging subject because each enantiomer has the same physical and chemical properties.

Some methods have been reported for enantiomeric separation, for example, preferential crystallization, chromatographic separation, enzyme-mediated resolution, and membrane-based separation (Xie et al. 2008). Among them, membrane-based method has some advantages over the other methods, such as low energy demand, continuous operation, and easy scale-up. Both liquid membrane and solid membrane have been applied to enantiomeric separation. The important factor of membrane-based enantioselective separation is the way how to give the function of chirality recognition to membranes. In the process using solid membranes, chirality recognition exists in main polymer chain, chiral polymer branch, and doped chiral selector or cavity formed by

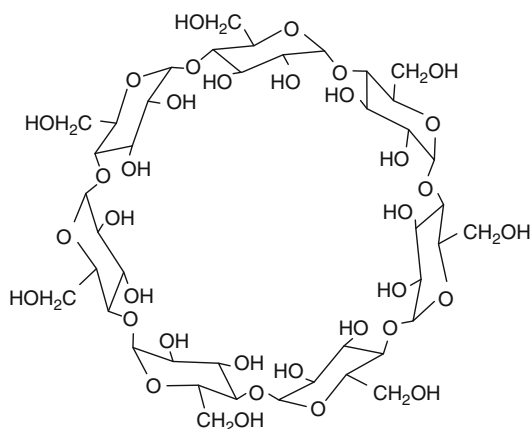


Supported Liquid Membrane for Enantioselective Separation, Fig. 1 Concept of transportation in SLM



Supported Liquid Membrane for Enantioselective Separation, Fig. 2 An example of chiral crown ether

molecular imprinting (Higuchi et al. 2010). On the other hand, in the separation with liquid membranes, enantioselective carriers are usually doped in the liquid membranes. In a supported liquid membrane (SLM), a liquid containing enantioselective carriers is impregnated into a porous support membrane. The separation concept in SLM process is shown in Fig. 1. On the membrane surface in the feed phase, a doped carrier combines with one isomer more preferentially than the other, and the carrier-isomer complex diffuses in the liquid membrane toward the strip phase. On the membrane surface of strip phase, the carrier releases the isomer. In the SLM process, the driving force is the concentration gradient of co- or counterions (indicated as X in Fig. 1) between feed and strip phases. Typical carriers used in SLM processes are crown ethers. Figure 2 shows the structure of one of crown



Supported Liquid Membrane for Enantioselective Separation, Fig. 3 β -Cyclodextrin

ethers that shows high enantioselectivity toward amino acids (Shinbo et al. 1993). Cyclodextrins are used as chiral carriers in aqueous SLM (Armstrong and Jin 1987). The molecular structure of β -cyclodextrin is shown in Fig. 3. The improvement of membrane stability is the key factor for the industrial application of SLM process (Kocherginsky et al. 2007).

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Supported Magnetic Ionic Liquid Membranes

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Supported ionic liquid membranes (SILMs) have been studied after immobilizing selected ionic liquids in polymeric or ceramic supports (Bara et al. 2009; Luis et al. 2009; Scovazzo et al. 2009). The influence of pore size and the stability evaluation regarding its hydrophobic or hydrophilic nature has been reported in the literature (Cserjesi et al. 2010; Neves et al. 2010).

Although SILMs present advantages due to the room temperature ionic liquid (RTIL) properties, their applications are still limited mainly associated to problems in their stability and/or long-term behavior (Criscuoli and Drioli 2008; Scovazzo 2009).

The magnetic behavior of a new generation of RTILs containing metal ions is recently under study in the literature. The combination of general RTIL features (e.g., chemical and thermal stability nonvolatile character and non-flammability) with new properties due to the incorporation of a metal ion has opened a new research area which is starting to attract a wide interest.

The MILs 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim][FeCl₄]) and 1-butyronitrile-3-methylimidazolium tetrachloroferrate ([n-bmim][FeCl₄]) were the first reported MILs to respond to an external magnet of about 0.55 T due to changes of its organization structure. MILs based on different transition metal ions such as iron, cobalt, manganese, and gadolinium showing a very interesting magnetic response with potential applications for magnetic and electrochromic switching have been reported, and the possibility of magnetic transport of a gas in MILs has been demonstrated, illustrated by the change in N₂ bubbles trajectory in the presence of a magnetic field (Hayashi and Hamaguchi 2004; Hayashi et al. 2006; DelSesto et al. 2008).

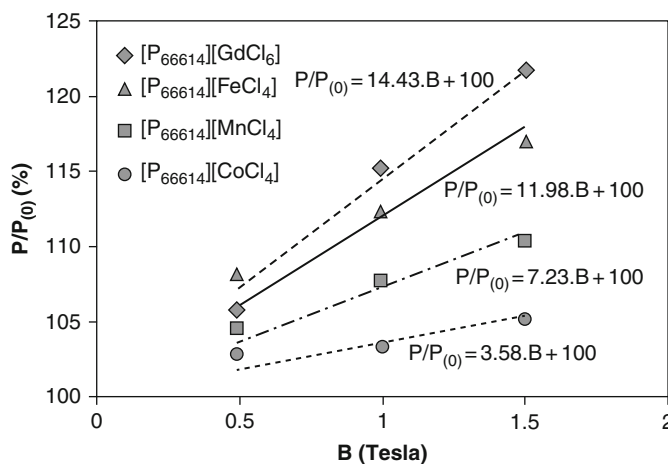
The application of an external magnetic field may modify the physicochemical properties, such as solubility or surface tension, by tuning the magnetic conditions. The dependence between the magnetic field intensity and the binary MIL/water equilibrium has been also observed, showing the increase of solubility of MILs in aqueous medium [16], which could improve the process efficiency. Other recent applications have shown a benzene solubility increase in the paramagnetic MIL [bmim][FeCl₄] when applying a rotational magnetic field or the improvement of phenolic compounds extraction in the MIL [3C₆PCl₄][FeCl₄] in the presence of a magnet (Deng et al. 2011).

The SMILMs were prepared using commercial microporous membranes from Millipore Corporation (USA). These supports are hydrophobic polyvinylidene fluoride (PVDF) membranes with a pore diameter of 0.22 μ m and an average thickness of 125 μ m. The immobilization procedure has been previously described [19]. To immobilize the MILs, the polymeric microporous membrane was introduced into a vacuum chamber for 1 h in order to facilitate the wetting. Afterward, drops of MILs were spread out at the membrane surface using a syringe keeping the vacuum inside the chamber, and, finally, the liquid excess on the membrane surface was wiped up softly with a tissue. The increase of weight and thickness was measured before and after the immobilization procedure (Albo et al. 2012; Ferguson and Scovazzo 2007; Condemarin and Scovazzo 2009).

The CO₂ permeability ratio (P(B)/P(0)) at different magnetic field intensities (B) (Fig. 1) shows the influence of an external magnetic field in the gas permeabilities of SMILMs. A recently published paper [20] has been able to show the influence of the external magnetic field application on gas permeability (CO₂, N₂, and air) through SMILMs in the range of 0–1.5 T. The gas permeability variation is related to the MIL viscosity change. Experimental results show that gas permeability increases as a function of the applied magnetic field depending on the magnetic ionic liquid (Santos et al. 2013).

Supported Magnetic Ionic Liquid Membranes,

Fig. 1 Relationship between the CO₂ permeability increases in SMILMs as a function of the magnetic field (*B*)



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Surface Analysis

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The surface analysis is the study of the membrane surface properties by means of surface analysis

Surface Analysis, Table 1 Main surface analysis techniques

Surface analysis techniques	Information
Attenuated total reflection Fourier transform infrared (ATR-FTIR)	The presence of membrane surface functionalities such as carbonyl, hydroxyl group, etc.
X-ray photoemission spectroscopy (XPS)	Chemical composition, variations in surface composition (Briggs 1998)
Static secondary ion mass spectrometry (SSIMS)	Chemical composition, variations in surface composition (Briggs 1998)
Energy dispersive x-ray spectroscopy (EDX)	Chemical composition, variations in surface composition
Optical microscopy (OM)	Topography, magnified images
Laser confocal scanning microscopy (LCSM)	Topography, images with increased optical resolution and contrast
Scanning electron microscopy (SEM)	Morphology, topography
Environmental scanning electron microscopy (ESEM)	Morphology, topography, micrographs of wet and/or uncoated samples
Contact angle measurement (CAM)	Surface energy, wettability
Atomic force microscopy (AFM)	Forces of the order of a few piconewtons surface roughness
Electrophoretic light scattering (ELS)	Surface zeta potential

techniques; they provide information on the morphology, topography, chemical composition, and wettability (Adamsons 2000; Bubert and Jenett 2002; Xu et al. 2009). The main used techniques and the information they give are listed in the following Table 1:

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Surface Charge

► Surface Charge Density

Surface Charge Density

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Synonyms

Membrane charge; Surface charge

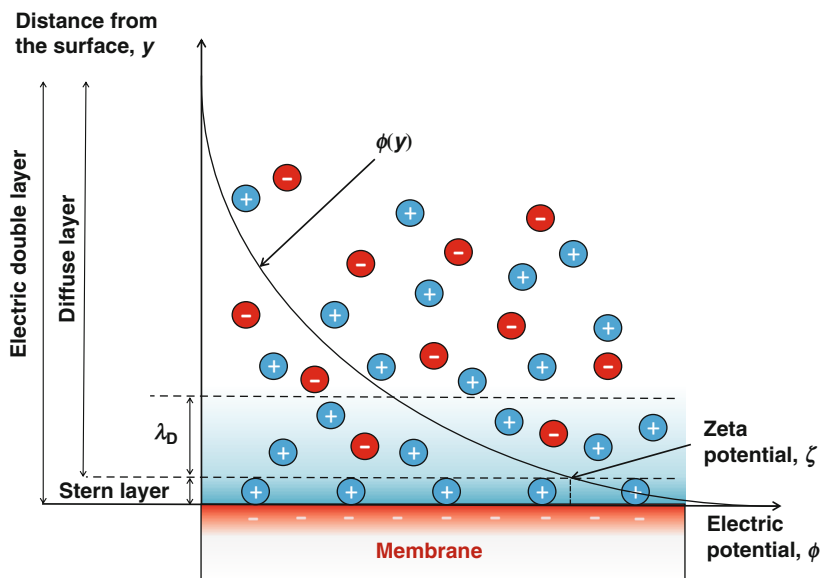
The **surface charge density** of a membrane is the total electric charge per unit of membrane surface area.

When a membrane surface is put in contact with a fluid containing charged species, several chemical interactions take place such as acid/base dissociation, ionization of functional groups, adsorption of ions on the membrane surface, and/or the partial dissolution of the membrane material (Cavaco Morão et al. 2006). Chemical equilibrium and the stabilizing effect of the solvent generally lead to the interface acquiring a net fixed electrical charge (most often negative) (Albrecht et al. 2013). The surface charge causes electrostatic attraction of counterions and the repulsion of co-ions, while the random thermal motion causes diffusion of the ions in the solution. These coupled phenomena create an electric double layer (EDL) with a net charge in the region near the membrane surface (Probstein 2005).

According to the Stern model (Stern 1924), the surface charge is distributed in three layers: (a) the

Surface Charge Density,

Fig. 1 Schematic of the electric double-layer structure, caused by a membrane surface charge density, illustrating the dependence of electric potential (ϕ) with distance from the surface (y)



intrinsic membrane charge on the membrane surface (σ_0); (b) the charge in the Stern layer (σ_s), related to counterions tightly bound to the surface; and (c) the charge of the diffuse layer (σ_d), which is required for overall electroneutrality:

$$\sigma_0 + \sigma_s + \sigma_d = 0 \quad (1)$$

The electric potential within the diffuse layer follows a Boltzmann distribution (Probstein 2005), as depicted in Fig. 1. The zeta potential (ζ), which is the potential at the boundary between the Stern layer and the diffuse layer, can be estimated through microelectrophoresis, electroosmosis, or streaming potential measurements (Bowen and Clark 1984). It is possible to calculate the diffuse layer charge density from zeta potential measurements by making use of the Gouy-Chapman equation (Cavaco Morão et al. 2006):

$$\sigma_d = \sqrt{2\varepsilon RT \sum_i C_i \left[\exp\left(-\frac{z_i F \zeta}{RT}\right) - 1 \right]} \quad (2)$$

where z_i and C_i are the valence and concentration of ionic species i , ε is the permittivity of the fluid, F is the Faraday constant, R is the universal gas constant, and T is the temperature.

The charge density in the Stern layer depends on the bulk solute concentration. Under

homogeneous adsorption, it can be described by a Langmuir isotherm (Molina et al. 1999):

$$\sigma_d = \frac{z_- e N X_- \exp\left(\frac{z_+ F \zeta - \Delta G_q}{RT}\right)}{1 + X_- \exp\left(\frac{z_+ F \zeta - \Delta G_q}{RT}\right)} \quad (3)$$

where z_- and z_+ are the valences of the anion and cation, respectively, e is the elementary charge, N is the total number of adsorption sites, X_- is the bulk anion molar fraction, and ΔG_q is the Gibbs free energy of chemical adsorption. Under heterogeneous adsorption, a Freundlich isotherm can be used to relate the charge density in the Stern layer to bulk concentration:

$$\sigma_d = a X_-^b \quad (4)$$

The surface charge density is a fundamental property of the membrane. It has a significant effect on its hydrophilicity, separation properties (Watanabe 1974), and fouling tendency (Breslau et al. 1980). Surface charge density and zeta potential vary with pH (Kim et al. 1996) and are dependent on the surface geometry (modifiable through casting), as there is a larger volume per unit surface area for a convex than a concave surface (Andelman 1995). Surface charge

density characterization is also useful in confirming surface modifications, such as in the development of highly selective membranes (Datta et al. 2010).

Cross-References

- [Electrical Double Layer](#)
- [Electrophoresis](#)
- [Membrane Charge](#)
- [Membrane Charge \(Zeta Potential\) Effect](#)
- [Use of Streaming Potential Measurements for Characterization of Both Membrane/Electrolyte Interface and Protein Fouling Effect](#)
- [Zeta Potential](#)

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Surface Modification: Chemical Treatment

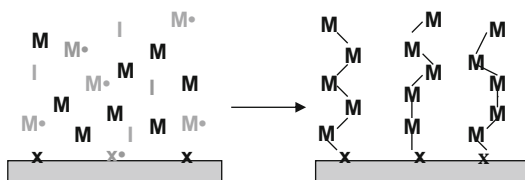
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Synonyms

Graft polymerization

Surface modifications have been widely used in the material- and polymer-based industries over past three decades [17]. It has the advantage of imparting the desired properties to the surface of interest while keeping the properties of bulk intact. Different innovative physical and chemical surface modification techniques have been introduced by various researchers in the field of polymers [17]. Over many years, graft polymerization (Fig. 1) has been studied in various fields of industrial applications, using different innovative techniques including different kinds of chemical and physical approaches. Modification via graft polymerization has many advantages over other methods, such as its ease of use and controllable introduction of graft chains to the surface with the bulk properties unchanged. Grafting of side chains can be performed in two ways, grafting-from and grafting-to methods [17]. In the former



Surface Modification: Chemical Treatment, Fig. 1 Schematic diagram of the graft polymerization process

method, the membrane surface consists of reactive radicals, while in the latter case, grafting chains carry the reactive radicals to initiate grafting. The procedures involved in grafting to surfaces are not straightforward enough for industrial applications, although the precise control of chain structure is in principle easier than with other methods [17]. Grafting can be achieved using different chemical techniques such as chemical oxidation, plasma discharge method and UV irradiation, and physical methods, such as radiation polymerization [17].

Belfer (Belfer et al. 2001) modified TFC membranes by redox polymerization using both sulfopropyl methacrylate (SPM), which gave a negative charge, and polyethylene glycol ester of methacrylic acid (PEGMA), which gave a neutral charge. Results of this test revealed that the modified membranes had an improved resistance to fouling, while salt rejection was similar when compared to the unmodified membrane. In addition, the foulant layer was easily rinsed clean, indicating that reversible fouling was prevalent for the modified membrane, whereas for the unmodified membrane, the foulant layer could not be removed. In a subsequent study, Gilron (Gilron et al. 2001) investigated the effect of graft polymerization of PEGMA, SPM, and 2-acrylamido-2-methyl propane sulfonate (AMPS) onto a variety of TFC polyamide membranes. The results showed that the permeability was reduced by no more than 25 % and salt rejection increased as much as 3 %. The modified membrane with the highest permeability was grafted with AMPS, and the modified membrane with the highest salt rejection was grafted with PEGMA. In addition, for modified membranes, the level of fouling by organic constituents was reduced, and the effectiveness of cleaning the modified membranes was greatly improved.

In order to reduce surface roughness and create a more hydrophilic membrane, Freger [56] investigated how graft polymerization of acrylic acid (AA) altered the surface structure of modified polyamide TFC NF membranes. The results of their analyses indicated that a thin layer of hydrophilic polymer may be deposited on the surface of the membrane. AFM analysis revealed that

polymer grafting reduced membrane surface roughness by a negligible amount, which indicated little improvement to fouling resistance occurred. In addition, the grafted polymer was shown to fill the pores of the porous support and led to reduced permeate production, which was a highly undesired result of membrane modification.

Graft polymerization of hydrophilic polymers has been extensively studied and is able to provide promising results. However, some drawbacks to this procedure can be substantial. Pore size reduction is a major consideration since it is directly capable of greatly reducing membrane productivity.

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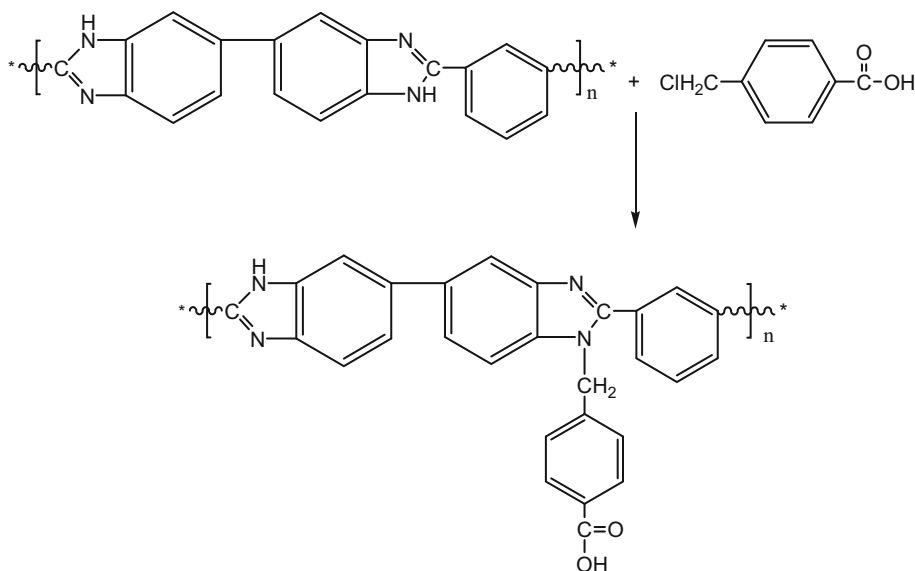
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Surface Modification: Introduction of Carboxyl Group

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In order to maintain membrane processes as economical alternatives to conventional water treatment technologies, they must produce a high-quality permeate at a high rate and be able to maintain that production for an extended period of time. However, the relationship between flux and selectivity along with fouling introduces a challenge that must be addressed for all membrane applications. There are three main areas of interest when it comes to improving membrane performance: (1) the synthesis process, (2) the



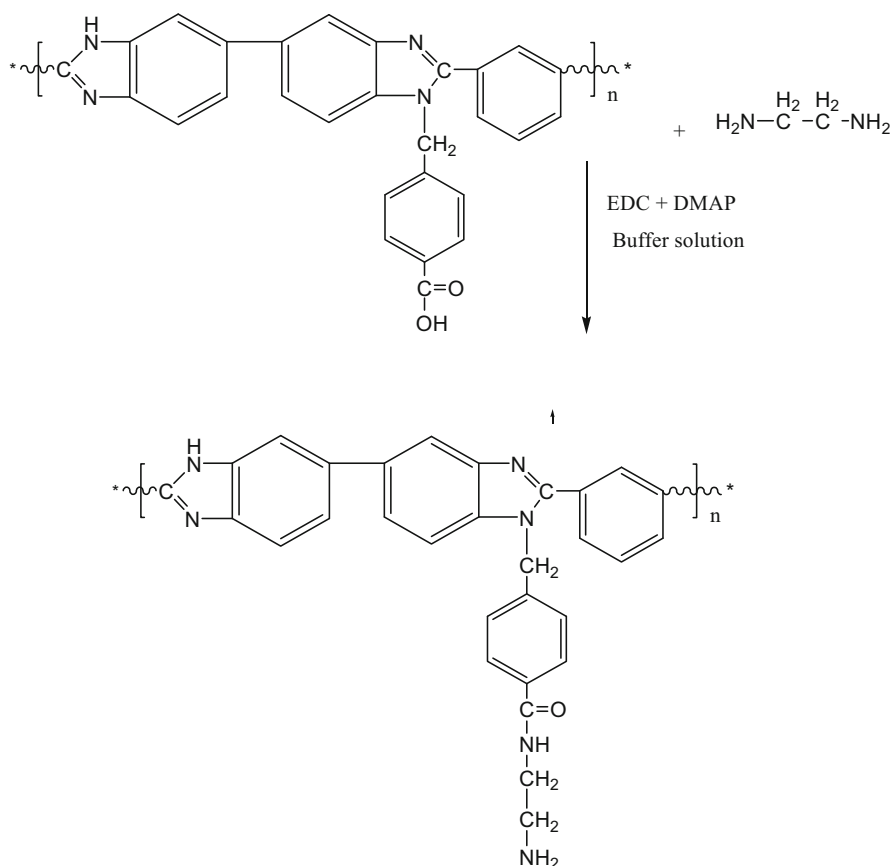
Surface Modification: Introduction of Carboxyl Group, Scheme 1 PBI activation with chloromethyl benzoic acid

application process, and (3) the post-synthesis modification. Synthesis process improvement involves the techniques, methods, and materials of the manufacturing processes to produce a high-performance membrane. The application process involves the specific operating parameters for a membrane system. These include selecting the raw water characteristics, operating pressure, and cleaning intervals to allow the system to operate at maximum efficiency. Post-synthesis modification involves modifying the membrane after the initial manufacturing process is complete.

There are several objectives for post-synthesis modification, or surface functionalization, which include, but are not limited to: enhance selectivity with focus on rejection of monovalent ions, increase flux of water, and enhance fouling resistance. Key targets for surface-modified groups include decreasing the hydrophobicity of the membrane, reducing the surface roughness, and altering the surface charge of the membrane. Many membranes are naturally hydrophobic due to the polymers that are used in the manufacturing process (including the PBI used for the NF membranes in this project). A drawback of a membrane exhibiting a hydrophobic nature is that it increases

the required transmembrane pressure (TMP) that must be utilized for operation, since the solvent (i.e., water) is repelled by the surface of the membrane. However, if a membrane can be rendered hydrophilic, the water is attracted to and transported through the membrane at a much faster rate, which reduces the required TMP for operation. In addition, many solutes found in feed waters are hydrophobic, so utilizing a hydrophilic membrane could increase the membrane's selectivity and fouling resistance. The severity of abiotic fouling is also directly linked to the membrane's surface roughness. Membranes with higher surface roughness have distinct peaks and valleys and are more susceptible to fouling, and with a reduction of roughness, foulants are less likely to adhere to the membrane. Functionalization with oligomers may reduce surface roughness and further improved fouling resistance.

Surfaces, such as polybenzimidazole (PBI), can be activated using a highly reactive chloride group, which reacted with the amide group of the PBI backbone to add carboxyl groups to the surface (Schemes 1 and 2). The carboxyl groups serve three purposes: (i) provide negative charge on surface since it can either protonate or



Surface Modification: Introduction of Carboxyl Group, Scheme 2 Modification using EDC chemistry

deprotonate based on the solution pH, (ii) provide hydrophilicity to surfaces, and (ii) act as a platform for subsequent functionalization.

Surface Modification: Wet Chemical Oxidation

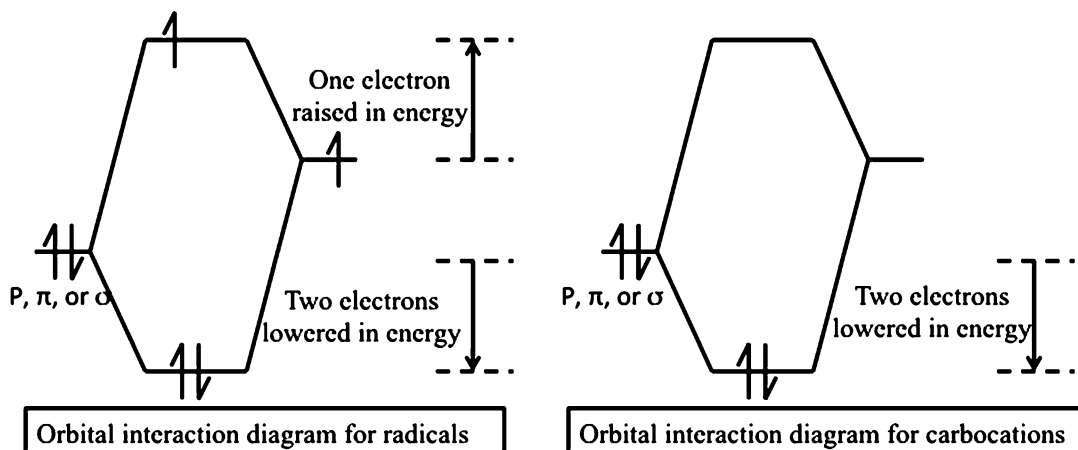
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Synonyms

Free radical polymerization

Surface modifications have been widely used in the material- and polymer-based industries over

the past three decades (Kato et al. 2003). It has the advantage of imparting the desired properties to the surface of interest while keeping the properties of bulk intact. Different innovative physical and chemical surface modification techniques have been introduced by various researchers in the field of polymers (Kato et al. 2003). Over many years, graft polymerization has been studied in various fields of industrial applications, using different innovative techniques including different kinds of chemical and physical approaches. Modification via graft polymerization has many advantages over other methods, such as its ease of use and controllable introduction of graft chains to the surface with the bulk properties unchanged. Grafting of side chains can be performed in two ways, grafting-from and grafting-to methods (Kato et al. 2003). In the former method, the membrane surface consists



Surface Modification: Wet Chemical Oxidation, Fig. 1 Orbital interaction chart for a carbon radical and a carbocation

of reactive radicals, while in the latter case, grafting chains carry the reactive radicals to initiate grafting. The procedures involved in grafting to surfaces are not straightforward enough for industrial applications, although the precise control of chain structure is in principle easier than with other methods (Kato et al. 2003). Grafting can be achieved using different chemical techniques such as chemical oxidation, plasma discharge method and UV irradiation, and physical methods, such as radiation polymerization (Kato et al. 2003), as previously discussed (see entry, Surface modification: chemical treatment). The part of the work described here focuses on free radical chain polymerization via chemical oxidation due to its nondestructive nature, relatively low economic feasibility, and ease of covalent bonding, which leads to the potential for in situ modification.

A radical is an atomic or molecular species having one or more unpaired electrons. Though they are electron deficient, they are uncharged resulting in different chemistries as compared to those of ionic or even electron species. Apart from very few stable radicals such as nitric oxide ($\text{NO}\cdot$), most radicals are very unstable and reactive making them suitable for initiating chemical reactions with typical stable polymeric surfaces. The amount of extra stabilization that adjacent lone pairs, π bonds, and σ bonds provide to

radicals is not as great as that which they provide to carbocations. The reason is that the interaction of a filled atomic molecular orbital with an empty atomic orbital (as in carbocations) puts two electrons in a molecular orbital of reduced energy. In contrast, the interaction of a filled atomic or molecular orbital with a half-filled atomic orbital (free radicals) puts two electrons in a molecular orbital of reduced energy and one electron in a molecular orbital of increased energy as shown in Fig. 1 (Jones 2005).

Pairs of electrically neutral free radicals can be formed via homolytic bond breakage that can be achieved by heating in nonpolar solvents or the vapor phase. All molecular species dissociate into radicals at elevated temperatures. Neutral radicals can also be produced in polar environments through oxidation processes (Jones 2005). Once the free radicals are formed on the membrane surface, due to their extreme reactivity, polymerization proceeds by coupling monomer chains to the membrane surface (Kato et al. 2003).

Radical activation of the polymer surface can be achieved by several of the previously mentioned methods such as chemical exposure, plasma treatment, and irradiation. In the current study, a chemical initiator, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), was used to produce free radicals on the CA membrane surface. Sodium persulfate, with its excellent solubility in aqueous media

and oxidizing nature, is a suitable agent for CA membrane surface activation and PEG chain propagation on the surface through the reaction between radical species formed as result of persulfate action.

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Surface Morphology

► Membrane Morphology

Surface Tension

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Surface tension: The term surface tension refers to the observation that the surface of a liquid behaves as though it were covered with a thin “skin” which resists attempts to puncture it. This property is caused by cohesion of similar molecules and is responsible for many of the behaviors of liquids. In the bulk of the liquid, each molecule is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. The molecules at the surface do not have other molecules on all sides of them and therefore are pulled inward. This creates some internal pressure and forces liquid surfaces to contract to the minimal area. Surface tension has the dimension of force per unit length or of energy per unit area. The two are equivalent. In SI surface tension is measured in N/m or in J/m² (although the more common units in cgs are dynes/cm or erg/cm², respectively).

Surfactants

► Amphiphilic Molecules

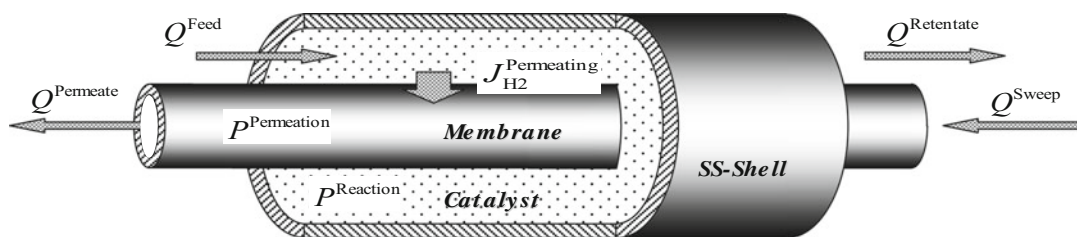
Sweep Gas in a Membrane Reactor

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The sweep gas is a gas present in the permeate side of a membrane reactor to lower the partial pressure of the permeating species and increase the driving force. This gas should be different from any species produced by the reaction, and permeating the membrane because of its back permeation into the reaction side deflects the reaction.

The permeation driving force, for any permeable species, is a function of the difference of chemical potential on both reaction and permeation sides of the membrane reactor. This is also valid for membrane reactors used for gas-phase reactions where the driving force can be increased operating on partial pressure both increasing the feed one and reducing permeate pressure of the specific chemical species.

Specifically, the partial pressure of a permeating species can be reduced in two ways: reducing the total pressure on the permeate side, applying a vacuum, for instance, and/or using a sweep gas on the permeate side. Both ones have the same effect since they increase the permeation driving force improving, as a consequence, the membrane reactor performance, that is, conversion and, if we're speaking about hydrogen production, the hydrogen recovery on the permeate side. However, depending on the used method, the permeate phase will have a very different composition. It will consist of the only permeable species in the case the vacuum is applied. In the other case, the concentration of the permeable species will be



Sweep Gas in a Membrane Reactor, Fig. 1 Scheme of a membrane reactor showing the four inlet/outlet stream, including the sweep gas one

lowered by the presence of the sweep gas; thus, another separation stage is required for purifying the permeate phase.

In a flow membrane reactor, the sweep stream can flow in co- or countercurrent with respect to the feed stream. The Fig. 1 shows the latter option in the case of methane conversion for hydrogen production.

Marigliano et al. (2003) demonstrated that in hydrogen production from methane steam reforming in palladium-based membrane reactor, a high hydrogen partial pressure on permeate led to a lower methane conversion, but a higher sweep gas flow rate reduces the hydrogen partial pressure increasing, in the meantime, the methane conversion.

The use of a sweep gas results in the dilution of the permeated species concentration (Marigliano et al. 2003). It is a drawback in many production cycles such as hydrogen production since the hydrogen permeating the membrane results diluted and requires a concentration. Few cases, for instance, are exceptions: (a) hydrogen produced for ammonia synthesis is good if diluted with nitrogen in a right feed ratio, and (b) the reaction conversion plays a more significant role than the permeated species.

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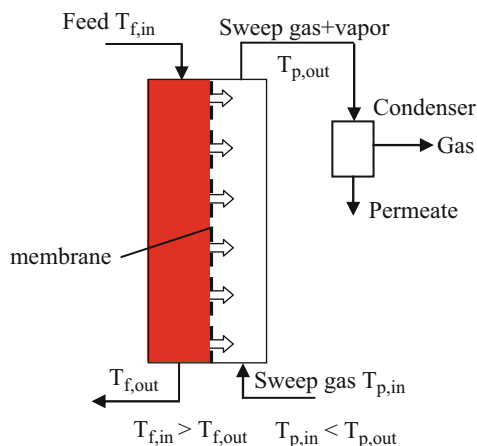
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Sweep Gas Membrane Distillation (SGMD)

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SGMD is a membrane distillation (MD) configuration in which a stripping gas is used as a carrier for the vapor transferred from a warm aqueous feed through a porous hydrophobic membrane. The nature of the membrane prevents from penetration of liquid into the pores; therefore, the liquid/vapor interface is formed at each pore entrance. The volatile molecules evaporate through the membrane pores, and a cold inert gas flowing along the other side of the membrane sweeps the permeate carrying it away from the module. The condensation of the vapor occurs in an external condenser (Fig. 1). The driving force for the mass transfer in SGMD is the difference in the partial pressure of volatile substances on both sides of the membrane. Since in MD heat is transferred from the feed side through the membrane, thus the sweep gas temperature increases considerably along a module. However, SGMD combines a relatively low conductive heat loss through the membrane with a reduced mass transfer resistance. Hence, the resulting high mass transfer coefficients provide higher permeate flux than that in direct contact membrane distillation (DCMD) (using the same membrane).



Sweep Gas Membrane Distillation (SGMD), Fig. 1 Schema of SGMD process

Membranes used in SGMD are porous and hydrophobic, similarly as in other MD configurations. Air, humid air, or dry nitrogen can be used as a sweep gas.

The permeate flux obtained in SGMD can be in the range from ca. 1 to 25 kg/m²h, depending on the membrane type, feed composition, and operating conditions (Khayet and Matsuura 2011). Nonvolatile species present in an aqueous solution are theoretically completely retained in the feed, whereas volatile organic substances are partially transferred through a membrane. The separation performance in SGMD is determined by a vapor/liquid equilibrium and depends mainly on a difference in volatility of components in a mixture. However, the differences in the diffusion rates of components through the gas in the membrane pores should be also taken into account.

For the case when SGMD is applied for treatment of an aqueous solution containing nonvolatile compounds and the permeate is swept away using air or any other neutral gas, the equations describing mass (J) and heat (Q) transfer in DCMD can be adapted (Khayet and Matsuura 2011):

$$J_w = B_w \left(p_{w,f}^0 a_{w,f} - p_{w,p} \right)$$

where B is membrane permeability (depends on membrane properties, e.g., thickness, porosity,

pore size) under the SGMD conditions, p is partial pressure, and a_w is water activity. The superscript 0 denotes pure water, and subscripts w , f , and p refer to water, feed, and permeate, respectively. The $p_{w,f}^0$ and $a_{w,f}$ depend on the feed temperature, whereas $p_{w,p}$ depends on the gas temperature at the membrane surface, respectively.

When volatile compounds are present in a feed, both the water vapor and the molecules of volatile compounds are transferred across a membrane. The separation factor of volatile compound i (α_i) can be calculated as:

$$\alpha_i = \frac{y_{i,p} / (1 - y_{i,p})}{x_{i,f} / (1 - x_{i,f})}$$

where $y_{i,p}$ and $x_{i,f}$ are molar fractions of i species in the gaseous permeate and liquid feed, respectively.

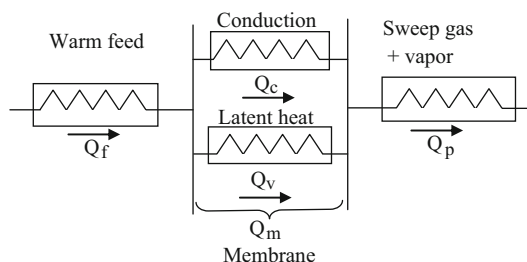
In this case the total SGMD permeate flux (J) (if coupling effects are not considered) can be written as:

$$\begin{aligned} J &= \sum_j B_j \left(p_{j,f}^0 a_{j,f} - p_{j,p} \right) \\ &= \sum_j B_j \left(p_{j,f}^0 \gamma_{j,f} x_{j,f} - f_{j,p} P \gamma_{j,p} \right) \end{aligned}$$

where $\gamma_{j,f}$, $x_{j,f}$, and $f_{j,p}$ are the activity coefficient, the mole fraction in the liquid and gas phase, and the fugacity coefficient of species j , respectively. The subscript j refers to all volatile compounds including water.

Various models were applied for description of mass transfer in SGMD. Nevertheless, it was usually concluded that the transport occurred according to a combined Knudsen/ordinary molecular diffusion mechanism.

The heat transfer in SGMD (Q) is described by the following steps: heat transfer through the liquid boundary layer on a feed side (Q_f), heat transfer through a membrane (Q_m) (through a membrane material and gas-filling pores (Q_c) and with permeate stream Q_v), and heat transfer through the gas boundary layer (Q_p) (Fig. 2).



Sweep Gas Membrane Distillation (SGMD),
Fig. 2 Heat transfer resistances in SGMD

Value of the permeate flux depends on the SGMD operation conditions, e.g., the inlet temperatures and the flow rates of both fluids, i.e., liquid feed and sweep gas, and membrane characteristics. The permeate flux is strongly dependent on a feed temperature because of exponential growth of vapor pressure with temperature. On the contrary, an increase in the sweep gas temperature leads to a decrease of the vapor pressure gradient thus the resultant permeate flux is lower. The major disadvantage of SGMD configuration is a very high increase of the gas temperature along a module.

The permeate flux is practically independent on the feed flow rate. The sweep gas flow rate is a very important parameter. An increase in the permeate flux with sweeping gas flow rate is caused by improved hydrodynamic conditions on the permeate side and a reduction of temperature polarization effect. The thermal efficiency of SGMD is higher than in DCMD because the heat loss by conduction through a membrane is lower (Charfi et al. 2010; Khayet and Matsuura 2011). It was found that the permeate flux is higher for membranes with larger pore size.

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Sweep Gas Membrane Distillation (SGMD) Applications

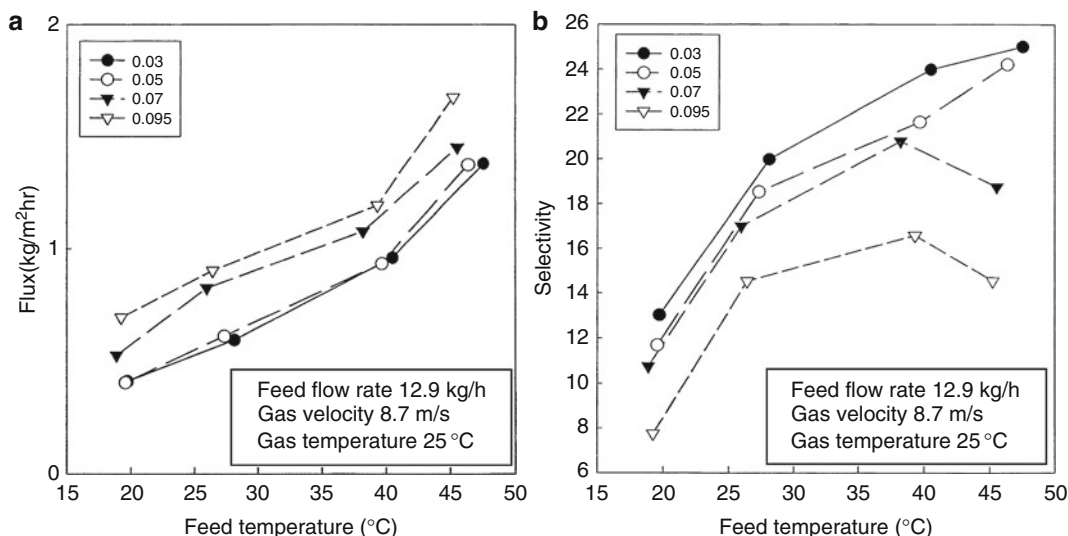
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SGMD is the least frequently used configuration of membrane distillation (MD) because the external condenser is required to collect the permeate. Moreover, a little amount of the permeate is collected by a large volume of a sweep gas. Therefore, the system design is complicated and rather expensive.

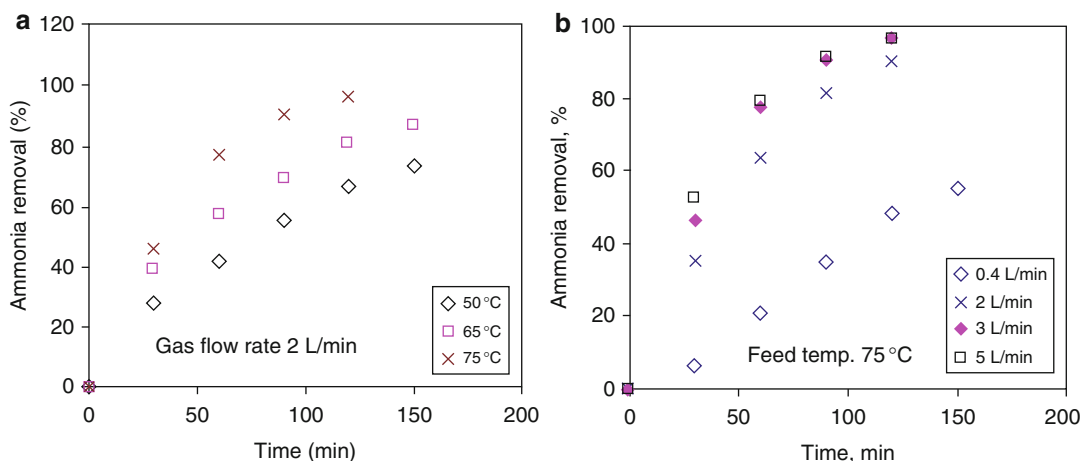
Similarly as the other MD configurations, the SGMD can be used to treat the solutions containing nonvolatile compounds, such as salts. The salt rejection is practically 100 % and high-purity water can be obtained. However, since the volatile species permeate through the membrane, a more profitable application of SGMD is the removal of volatile organic substances (esters, ethers, chlorinated hydrocarbons, aromatic compounds) or dissolved gases from aqueous solutions. Thus, SGMD can be applied in chemical and petrochemical industries, in biotechnology, or in environmental engineering, where the organic substances have to be recovered/removed from very diluted solutions. Moreover, SGMD can be applied in the cases where DCMD cannot be used due to the risk of the membrane wetting.

Laboratory-scale studies have demonstrated a high potential of SGMD for removal of organic volatile compounds such as ethanol, isopropanol (IPA), and acetone from wastewater (Khayet and Matsuura 2011). A novel SGMD-based micro-separator has been studied for the separation of a mixture of methanol and water. A bioreactor combined with SGMD for ethanol production was also proposed, in order to enhance the ethanol productivity as well as to eliminate the fermentation inhibitors. The produced ethanol was free of bacteria, nutrients, and metabolites (He et al. 2012).



Sweep Gas Membrane Distillation (SGMD) Applications, Fig. 1 (a) SGMD flux and (b) IPA selectivity as a function of feed temperature at various feed concentrations

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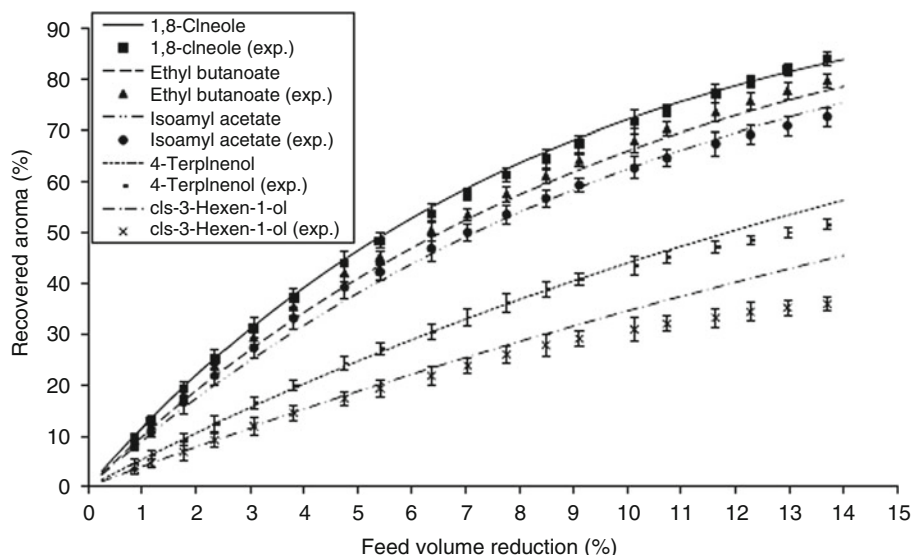
Sweep Gas Membrane Distillation (SGMD) Applications, Fig. 2 (a) Effect of feed temperature and (b) flow rate of sweep gas on ammonia removal using SGMD, feed

flow rate 250 mL/min (Reprinted from Xie et al. 2009, copyright (2009), with permission from Elsevier)

SGMD was applied for treatment of IPA aqueous solutions (below 10 wt.%). The influence of feed temperature on the selectivity and permeate flux is presented in Fig. 1. It was found that the selectivity decreased with an increase of sweep gas flow rate and with IPA concentration in a feed. Moreover, MgCl₂ addition to the feed increased

significantly IPA selectivity, with small reduction of the total permeate flux (Lee and Hong 2001).

High effectiveness (97 %) of SGMD during the removal of ammonia from synthetic industrial wastewater (100 mg/l, pH 11) was also found (Fig. 2). At higher feed temperature, the permeate flux significantly increased, but the selectivity of



Sweep Gas Membrane Distillation (SGMD) Applications, Fig. 3 The experimental results and theoretically predicted values of aroma fractions recovery by SGMD

(Reprinted from Bagger-Jørgensen et al. 2011, copyright (2011), with permission from Elsevier)

ammonia was reduced. For membranes with smaller thickness and larger pore size, the mass transfer coefficient of ammonia was higher, whereas its selectivity was lower. The pH of ammonia solution was very important for its separation (Xie et al. 2009).

Another SGMD application can be an industrial fruit juice processing. Successful experiments were carried out using SGMD for the concentration of sucrose solutions as a model fruit juice (Khayet and Matsuura 2011). SGMD was also used for the recovery of black currant and cherry juice aroma compounds from a model solution and for the retention of anthocyanins in the juice. An increase in the feed temperature improved the aroma flux; thus, their concentration in the permeate was elevated. The highest concentration factors for highly volatile aroma compounds were in the range of 12.1–9.3 (black currant juice) and 16.3–13.0 (model solution). In the case of a black currant juice, the amount of recovered aroma was 73–84 vol.% for the highly volatile compounds (Fig. 3). However, during the concentration of juice, a part of anthocyanins and polyphenols in black currant juice was lost due to

the degradation of anthocyanin by oxidation (Bagger-Jørgensen et al. 2011).

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Synthetic Biomembrane

► Bioartificial Synthetic Membrane

Tapping Mode

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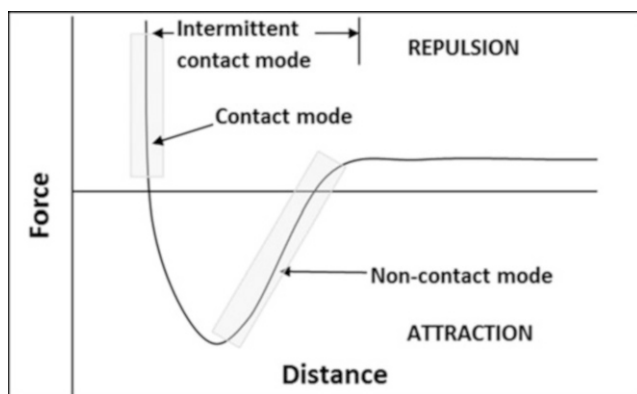
There are many different imaging modes available for the AFM, providing a range of different information about the sample surfaces being examined. However, for simplicity the most common modes will be considered here. In Fig. 1 the force regimes under which the main imaging modes occur are illustrated schematically. In this figure the interaction forces are sketched as the probe approaches and contacts the surface, with distance increasing to the right. At large separations there are no net forces acting between the probe and sample surface. As probe and surface approach each other, attractive van der Waals interactions begin to pull the probe toward the surface. As contact is made, the net interaction becomes repulsive as electron shells in atoms in the opposing surfaces repel each other. In this diagram the repulsive forces are shown as being positive and attractive forces negative.

Intermittent, or tapping, mode of imaging was developed (Hansma et al. 1993, 1994; Zhong et al. 1993) to overcome the limitations of contact mode imaging (Bowen and Hilal 2009). Here the cantilever is allowed to oscillate at a value close to

its resonant frequency. When the oscillations occur close to a sample surface, the probe will repeatedly engage and disengage with the surface, restricting the amplitude of oscillation. As the surface is scanned, the oscillatory amplitude of the cantilever will change as it encounters differing topography. By using a feedback mechanism to alter the z height of the piezo and maintain constant amplitude, an image of the surface topography may be obtained in a similar manner as with contact mode imaging. In this way lateral forces as the probe is scanned across the surface are greatly reduced, compared with the contact mode.

When using tapping mode in air, capillary forces due to thin layers of adsorbed water on surfaces have to be overcome, as well as any other adhesive forces which may be present. If the restoring force of the cantilever due to its deflection is insufficient to overcome adhesion between the probe and the surface, then the probe will be dragged along the surface in an inadvertent contact mode. As a result, for this mode in air, the spring constants of AFM cantilevers are by necessity several orders of magnitude greater than those used for either tapping mode in liquid or contact mode (typically in the range of $0.01\text{--}2\text{ N m}^{-1}$ for contact mode to $20\text{--}75\text{ N m}^{-1}$ for tapping in air).

As surfaces with different mechanical and adhesive properties are scanned, the frequency of oscillation will change causing a shift in the phase signal between the drive frequency and the frequency with which the cantilever is actually



Tapping Mode, Fig. 1 Diagram illustrating the force regimes under which each of the three most common AFM imaging modes operate. Contact mode operation is in the repulsive force regime, where the probe is pressed against the sample surface, causing an upward deflection of

the cantilever. Noncontact mode interrogates the long range forces experienced prior to actual contact with the surface. With intermittent contact, or tapping mode, the probe is oscillated close to the surface where it repeatedly comes into and out of contact with the surface

oscillating (Schmitz et al. 1997; McLean and Sauer 1997). This phenomenon has been used to produce phase images alongside topographic images, which are able to show changes in the material properties of the surfaces being investigated. However, while the qualitative data this provides is useful, it is difficult to extract quantitative information from the phase images due to it being a complex result of a number of parameters, including adhesion, scan speed, load force, topography, and the material, especially elastic, properties of the sample and probe (McLean and Sauer 1997; Loos 2005).

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Temperature Polarization

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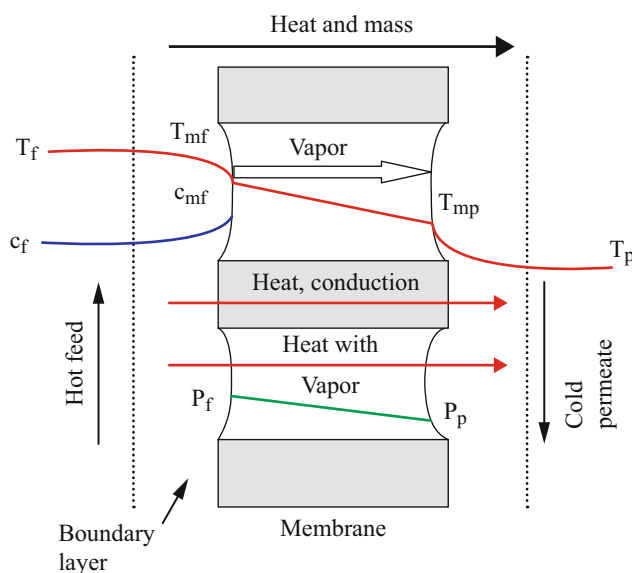
In the membrane distillation (MD) process, mass and heat transfer through a hydrophobic microporous membrane occurs simultaneously. The mass transfer proceeds through the membrane pores, whereas the heat is transferred both through the pores (with permeate flux) and across the membrane material.

According to the mechanism of MD, water and volatile solutes present in the feeding solution evaporate from the liquid–vapor interface on the

Temperature

Polarization, Fig. 1 Heat

and mass transfer through the membrane in DCMD configuration



feed side of a hydrophobic membrane. The vapor is transferred through the membrane pores and subsequently is either condensed in the stream of cold distillate flowing along the membrane or removed from a membrane module on the distillate side.

Since the mass transfer in MD occurs in a vapor form, the energy for water evaporation has to be supplied from the hot feed to the liquid-membrane interface. When the vapor is condensed at the vapor-liquid interface on the cold side of the membrane, the energy (heat) is released. Moreover, a part of energy accumulated in the hot feed is transferred across the membrane material and the gas trapped in the pores. Around 50–80 % of energy is consumed as the latent heat for the water vapor production, whereas 20–40 % is lost by conduction through the membrane (Alkhudhiri et al. 2012). Thus, the temperatures in the bulk feed and permeate solutions (T_f and T_p , respectively) differ from the corresponding temperatures at the membrane/solution interface where vapor-liquid transition occurs (T_{mf} and T_{mp}), which is presented in Fig. 1. This phenomenon is termed as **temperature polarization (TP)**. A decrease of temperature on the feed side reduces the partial vapor pressure being in equilibrium with the liquid phase, whereas higher temperature on the permeate side increases the

partial pressure which results in a reduction of both the driving force (i.e., vapor pressure difference ($p_f - p_p$)) and the permeate flux through MD membranes. The boundary layers are formed at the membrane surfaces both on the feed and permeate sides. This causes an additional resistance, besides a membrane resistance, and is considered as the limiting factor of the mass transport efficiency (Khayet 2011).

Regardless of MD configuration, the mass and heat transport through the membrane as well as the effects of temperature boundary layers at the membrane surfaces which affected the magnitude (extent) of **TP** should be taken into account. The most severe, negative influence of **TP** can be expected in DCMD, where a substantial resistance of the boundary layers present in a liquid form on the both sides of the membrane can be observed.

In the vacuum membrane distillation (VMD) process, the vacuum provides insulation against conductive heat loss through the membrane, and the boundary layer resistance on the permeate side is negligible. In the air gap membrane distillation (AGMD), a stagnant air is introduced between the membrane and the condensation surface which reduces a heat loss by conduction. However, an additional resistance to mass transfer is generated. In sweep gas membrane distillation (SGMD), an inert gas is used to sweep the vapor at the

permeate side of a membrane. The gas barrier reduces the heat loss, but the conditions are not stationary, and the mass transfer coefficient increases (Alkhudhiri et al. 2012).

TP in MD can be reduced by using appropriate membranes, which are characterized by:

- As low as possible, thermal conductivity of the membrane material to reduce heat loss through conduction
- Optimized thickness, because it is inversely proportional to the rate of mass and heat transport through the membrane
- High porosity, since the conductive heat transfer coefficients of the gases entrapped in the pores are an order of magnitude smaller than those of the used membrane materials

TP can be also diminished when the flow rate of streams along the membrane surface reduces the boundary layer thickness.

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Temperature Polarization Coefficient (TPC)

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In all membrane distillation (MD) configurations, the mass and heat transfer takes place simultaneously. In the process the water vapor is transferred through a porous hydrophobic membrane. In order to achieve evaporation of water at the membrane-liquid interface, the heat has to be

supplied from the warm feed. In direct contact membrane distillation (DCMD), the vapor condenses at the cold membrane-liquid interface, and the heat is released to a cold distillate. This creates temperature gradients in the boundary layers adjacent to both sides of the membrane. The temperatures in the bulk solution (T_f and T_p) are different from the corresponding values on the membrane surfaces (T_{fm} and T_{pm}). The heat transfer across the boundary layers is often considered as the limiting factor for mass transfer in DCMD. The temperature polarization coefficient (TPC) (Θ) is generally used as a measure of the magnitude of the boundary layer resistance in relation to the total heat transfer resistance. TPC can be also written as a function of the heat transfer coefficients in the thermal boundary layers:

$$\begin{aligned}\Theta &= (T_{fm} - T_{pm}) / (T_f - T_p) \\ &= 1 - H/h \text{ where } 1/h = 1/h_f + 1/h_p\end{aligned}$$

The h_f and h_p are the heat transfer coefficients in the feed and permeate boundary layers, respectively, and H is the global heat transfer coefficient of the MD process.

TPC indicates a reduction in the effective driving force (vapor pressure difference through the hydrophobic membrane) and has a negative influence on DCMD productivity.

When the thermal boundary layer resistances are reduced, the temperature differences between the liquid-vapor interfaces and the bulk temperatures become close to each other, and TPC approaches to 1. This value can be achieved in a properly designed module, in which the only limitation is mass transfer. For a poorly designed module with high heat resistance of boundary layers, the value of Θ approaches to zero and the process is limited by heat transfer. Usually, for the appropriate designed systems, the value of Θ is in the range of 0.4–0.7.

The performance of DCMD module can be improved by the application of turbulent flow promoters or net spacers to minimize the heat resistance and to increase the heat transfer coefficients of the boundary layers (Khayet and Matsuura 2011). Generally, TPC increases with increasing

feed and permeate flow rates and is reduced with increasing temperature of a feed. Moreover, this coefficient strongly depends on the membrane characteristics. The driving force of MD is decreased by both temperature polarization and concentration polarization. Therefore, they can be combined in one coefficient called the vapor pressure polarization coefficient (Khayet 2011).

TPC defined and calculated for DCMD can be also applied to other MD configurations. In sweep gas membrane distillation (SGMD) and air gap membrane distillation, the heat transfer coefficient on the permeate side is much smaller than that on the liquid side. Therefore, in SGMD the flow rate of sweeping gas controls the process. In vacuum membrane distillation, the boundary layer resistance on the permeate side is negligible. In this case TPC depends on the heat transfer coefficient in feed boundary layer and increases with a membrane permeability (pore size and porosity).

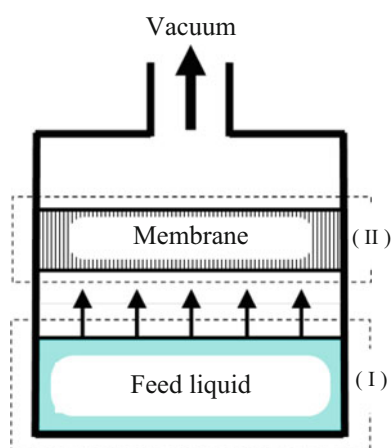
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Temperature-Difference-Controlled Evapomeation (TDEV)

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As mentioned in the heading of “Evapomeation (EV),” a new EV method for membrane separation that improves upon the shortcomings of pervaporation while keeping the advantages of this technique was developed (Uragami et al. 1988; Uragami and Saito 1989; Uragami 1991, 1993a, b, 1998, 2005, 2006a, b; Uragami 1994). In EV, the temperatures of the feed liquid



Temperature-Difference-Controlled Evapomeation (TDEV), Fig. 1 Principle of temperature-difference-controlled evapomeation (TDEV)

(I) and the membrane surroundings (II) are controlled, and consequently a differential between these temperatures can be established, as shown in Fig. 1. Such an EV method, in which this temperature difference is controlled, is called “temperature-difference controlled evapomeation” (TDEV) (Uragami 1998, 2005, 2006a, b, 2008, 2011; Uragami and Morikawa 1987, 1992; Uragami and Tanaka 1991, 1993, 1994; Uragami and Shinomiya 1991, 1992; Uragami et al. 2002).

In TDEV, when the temperature of the feed liquid was kept constant at 40 °C and the temperature of the membrane surroundings was changed for an aqueous dilute ethanol solution through a dense poly(dimethylsiloxane) (PDMS), the permeation rate decreased but the ethanol to a temperature less than the temperature of the feed liquid concentration in the permeate increased with lowering of the temperature in the membrane surroundings. The decrease in the permeation rate can be attributed to lowering the motion of both the permeating molecules and polymer chains consisting the PDMS membrane. On the other hand, the increase in the ethanol/water selectivity is explained as follows. At first, ethanol and water molecules are vaporized from the feed mixture at higher temperature. When those vaporized molecules come close to the membrane surroundings kept at a lower temperature, the water molecules

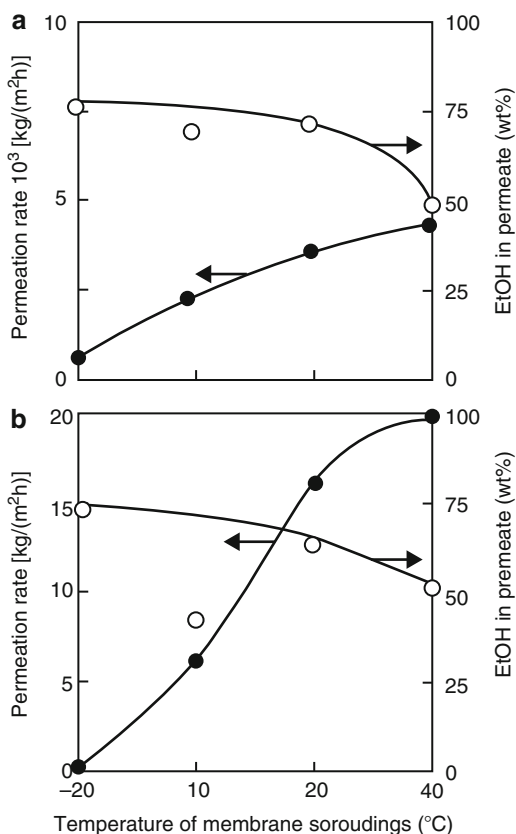
Temperature-Difference-Controlled Evapomeation (TDEV), Table 1 Effect of the freezing point on the selectivity of the permeant in the organic liquid mixtures through polymer membranes in TDEV

Membrane	Chitosan	PVC	PDMS
Freezing point of permeant	(CH ₃) ₂ SO/ H ₂ O 18.5 °C > 0 °C	CH ₃ COOH/ H ₂ O 16.7 °C > 0 °C	C ₂ H ₅ OH/ H ₂ O −114.4 °C < 0 °C
Selectivity	H ₂ O	H ₂ O	C ₂ H ₅ OH

are more aggregated than the ethanol molecules (because the freezing points of water and ethanol are 0 and −114.4 °C, respectively). It is very difficult for these aggregated water molecules to be incorporated into the dense PDMS membrane and diffuse through the dense PDMS membrane. However, the ethanol molecules are not aggregated in the range of the temperature in the membrane surroundings under these permeation conditions. The increase in the ethanol/water selectivity is due to the aggregation of water molecules and is significantly governed by the degree of aggregation of the water molecules.

In Table 1, the effect of the freezing point of the permeant in aqueous organic liquid mixtures on the selectivity through some polymer membranes in TDEV in which the feed liquid was kept constant and the temperature of membrane surroundings was changed is summarized. As can be seen from Table 1, the permeant having a lower freezing point in the feed mixture is selectively permeated. In addition, when the membrane has a stronger affinity to the preferentially permeating mixture component, an increase in selectivity can result in TDEV.

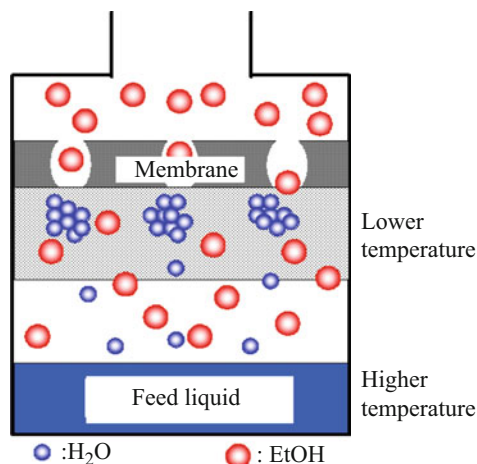
Figure 2 shows the effect of the temperature of the membrane surroundings on the permeation rate and the ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol through a dense PDMS membrane (a) and a porous PDMS membrane (b) in TDEV. In Fig. 2, the temperature of the feed solution is kept constant at 40 °C, and the temperature of the membrane surroundings was changed. As shown in Fig. 2a, b, the tendency of the decrease in the permeation rate decreased, and the increase in



Temperature-Difference-Controlled Evapomeation (TDEV), Fig. 2 Comparison of the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol of a dense PDMS membrane (a) and a porous PDMS membrane (b) in TDEV. Feed liquid is aqueous solution of 10 wt.% ethanol (40 °C)

the ethanol/water selectivity with lowering temperature of the membrane surroundings through these two PDMS membranes was very similar. In spite of the fact that the ethanol/water selectivity in these PDMS membranes was almost equal, the permeation rates through these PDMS membranes were remarkably different, i.e., the permeation rates in a porous PDMS membrane were higher by three orders of magnitude than those of a dense PDMS membrane.

A remarkable difference in the permeation rate between dense and porous PDMS membranes can be attributed to the fact that the permeation through a dense PDMS membrane is due to the



Temperature-Difference-Controlled Evapomeation (TDEV), Fig. 3 Tentative mechanism of the concentration of aqueous ethanol solutions through porous PDMS membrane in TDEV

solution-diffusion model (Binding et al. 1961; Aptel et al. 1974) and that through a porous PDMS membrane is pore flow based on, as shown in Fig. 3.

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Temporary Liver Support Systems

► Bioartificial Liver Support System (BLSS)

Tensile Strength

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Tensile strength, often indicated as **ultimate tensile strength** or **ultimate strength**, is the maximum stress that a material can withstand while being stretched before failing or breaking.

The tensile strength of a membrane is usually measured by a tensile tester registering tensile stress versus strain (i.e., extension per original length) until failing or breaking. At a given temperature the specimen is clamped between two grips and stressed by moving the mobile grip at constant rate of extension, while the fixed grip is connected to a force transducer (Fig. 1).

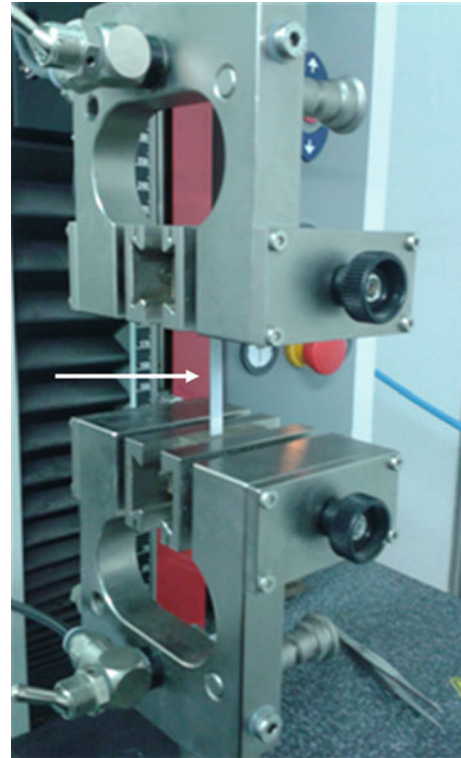
The tensile strength (TS) is calculated by

$$TS = \frac{F_{\max}}{S}$$

where TS is the tensile strength (Nm^{-2} or Pa); $F_{\max}$ is the maximum stress before specimen failing or breaking (N); S is the initial cross section area of the sample (m^2), i.e., the product of membrane thickness for sample wide. The tensile strength is often reported in Nmm^{-2} or MPa.

Observing a stress/strain curve (Fig. 2) it is possible to distinguish two different regions:

- The region of elastic deformation (ER) corresponding to the linear portion of the curve (slope constant), where a reversible deformation of the material occurs and ends at the elastic limit (D, Fig. 2), at which the slope of the curve starts to decrease.



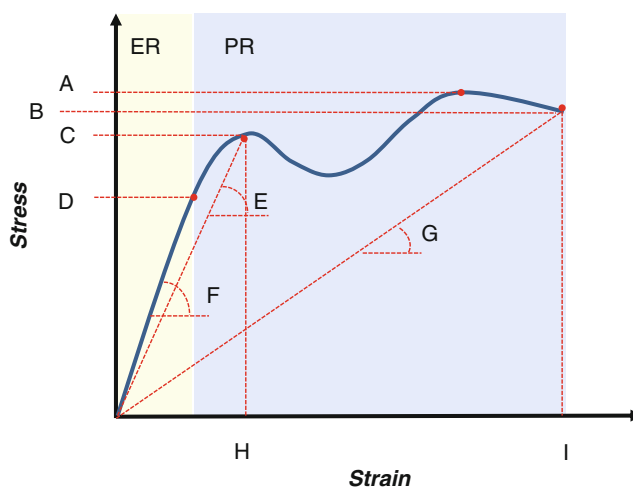
Tensile Strength, Fig. 1 Image of a membrane specimen clamped between two grips (indicated by a white arrow) during a stress–strain elongation test

- The region of plastic deformation (PR); after the elastic limit, where the slope of the curve decreases considerably and for some materials it resets very quickly in correspondence of the yield stress (C); for others it continues to decrease until the break in the sample (B) which can also take place by stress lower than the maximum registered during the test.

In the elastic region, once stress is removed, the sample returns to original size/shape. In the plastic region permanent deformations are induced by the applied stress.

In addition to tensile strength (A, Fig. 2), other mechanical parameters that can be obtained from a stress-strain test are:

- Breaking point (B, Fig. 2; [Nm^{-2}]): is the strain registered at the failure or breaking of the specimen.



Tensile Strength, Fig. 2 Typical stress–strain curve and the main parameters that can be obtained: *A*: tensile strength (Nm^{-2}); *B*: breaking point (Nm^{-2}); *C*: yield strength (Nm^{-2}); *D*: elastic limit (Nm^{-2}); *E*: modulus of yield (Nm^{-2}); *F*: modulus of elasticity or Young's modulus

(Nm^{-2}); *G*: modulus of rupture (Nm^{-2}); *H*: elongation at yield (%); *I*: elongation at break (%). The yellow zone correspond to the elastic region (ER) and the blue zone to the plastic region (PR)

- Yield strength (*C*, Fig. 2; [Nm^{-2}]): is the stress which corresponds to the first significant drop of the stress–strain curve, when an increase in the deformation does not correspond to a linear increase in stress.
- Modulus of yield (*E*, Fig. 2; [Nm^{-2}]): is the slope of the line joining the origin of the diagram with the yield strength point.
- Modulus of elasticity or Young's modulus (*F*, Fig. 2; [Nm^{-2}]): is the ratio of the stress and the corresponding strain in the elastic region. It represents a measure of the elasticity: the higher the Young's modulus, the greater the rigidity of the sample.
- Modulus of rupture (*G*, Fig. 2; [Nm^{-2}]): is the slope of the line joining the origin of the diagram with the breaking point.
- Elongation at yield (*H*, Fig. 2; [%]): is the increase in elongation (deformation in percentage or relative) at the yield strength point.
- Elongation at break: is the increase in elongation at the rupture of the specimen (*I*, Fig. 2; [%]).

Tensile strength is one of the key factors that influence the industrial application of the membranes because of its impact on long-term

performance of the same. During their operative life, membranes undergo continuous mechanical solicitations during filtration operations, as well as cleaning procedures (e.g., backwashing) and a high tensile strength is a desirable property to increase membrane durability.

The addition of inorganic nanoparticles (e.g., silica, Fe_3O_4 , ZrO_2 , TiO_2 , CdS) to polymeric membranes can cause an increase in tensile strength to some extent because the free motion of polymeric chains can be partly restricted by the intermolecular forces between the polymeric chains and the inorganic nanoparticles (Ng et al. 2013). In particular the exceptional tensile strength of graphitic nanostructures like carbon nanotubes and graphene has been motivating an increasing interest to reinforce polymeric membranes with these additives (Spitalskya et al. 2010; Kuilla et al. 2010; Fontananova et al. 2015). Tensile strengths of carbon nanotubes range from 60 to 150 GPa while the values for graphene monolayers are around 130 GPa, versus typical values of 10–30 MPa of numerous organic polymers (e.g., high-density polyethylene and natural rubber).

Tensile strength can also be enhanced by a chemical and/or physical cross-linking of the

membranes. Of course not only composition but also membrane structure influences the resulting tensile strength.

In the case of crystalline or semicrystalline membrane materials also crystal form, crystallinity, and crystalline morphology can have a relevant impact on the tensile strength (Liu et al. 2013).

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Ternary Pd-Alloy Membranes

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Palladium (Pd) has high solubility and diffusivity of hydrogen and shows therefore great promise as a membrane material for medium to high temperature hydrogen separation (250–550 °C). In pure Pd, however, an α -to- β -hydride phase transition may occur in hydrogen below about 290 °C, and only a few cycles through this transition make the material brittle and must be avoided. By alloying Pd with different elements, the phase transition can be suppressed, and the majority of the work

related to Pd-alloy membranes applies particularly alloys with 20–30 wt.% Ag and 40 wt.% Cu. The drawback is, however, that these alloys are to various degrees prone to poisoning by CO- and sulfur-containing gases leading to reduced H₂ flux or even to a complete membrane failure. Research therefore currently focuses on developing more advanced ternary or quaternary alloys that may be needed to improve the mechanical, thermal, and chemical stability of Pd-based membranes.

The main problems with membrane reliability are related to their corrosion resistance and structural changes that occur during operation. Palladium and Pd-alloys have therefore been alloyed with additional other metals, including Ru, Mo, W, Y, Ta, V, Rh, Nb, Cr, Ni, and Fe, to obtain greater mechanical strength and to inhibit undesired grain growth resulting in an increased temperature stability. Doping Pd with higher melting point metals (such as Ru or Pt) seems to enhance the thermal stability of the membrane. In terms of corrosion resistance, various approaches involving ternary Pd-alloys are being followed. Fcc Pd-Cu membranes are known for their sulfur tolerance but are less permeable than Pd. Several studies have therefore focused on improving the hydrogen flux through Pd-Cu membranes by adding a third element. In this respect, Ag is most particularly interesting since Pd-Ag has a higher hydrogen permeability compared to pure Pd. Another approach is to alloy the high-flux Pd-Ag alloy membrane with ternary elements to enhance the sulfur tolerance without significantly reducing the high permeability of this alloy. The Pd-Ag-Au alloy developed along this route displayed higher initial H₂ permeability than pure Pd and, consistent with resistance to bulk sulfide formation, lower permeability loss in H₂S than pure Pd. This indicates that the addition of small amounts of Au to the high-flux Pd-Ag alloy membrane improves the sulfur tolerance of this alloy and that this could be an interesting approach in the development of high-flux Pd-based alloy membranes with improved sulfur tolerance. Still, however, flux targets remain a challenge for new alloys in large-scale applications in the presence of sulfur impurities.

Tetrazole Group

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Tetrazoles are a class of heterocyclic compounds consisting of a five-member ring of four nitrogen and one carbon atom. The chemical formula for simplest tetrazole is CN_4H_2 and the chemical structure is represented in Fig. 1.

Tetrazoles have wide range of applications which are currently receiving considerable attention (Butler 1996); therefore, the literature on tetrazole is expanding rapidly. This functional group has a role in coordination chemistry as a ligand (Du et al. 2011), as well as in various materials sciences applications including photography, energetic materials, and membranes (Gomes 2012; Herr 2002; Miyata et al. 2004, 2005). Tetrazole and its derivatives such as 5-aminotetrazole are sometimes used as a component of gas generators in automobile airbags. Extensive work has also been carried out in the field of medicinal chemistry, where tetrazoles are frequently used as metabolically stable surrogates for carboxylic acids (Lin 2005; Pu et al. 2008).

One of the recent researches in the development of novel microporous organic polymers (MOPs) represented that by the introduction of tetrazole groups into highly microporous polymeric frameworks resulted the favorable CO_2 sorption with superior affinity in gas mixtures and selective CO_2 transport by presorbed CO_2 molecules that limit access by other light gas molecules. This proves the importance of tetrazole groups in designing MOP membrane materials for economic CO_2 capture processes (Singh et al. 2006). Proton-conductive and particularly anhydrous proton

conductivity of poly(5-vinyltetrazole)-based composite membranes were also evaluated and found to be efficient not only for intermediate temperature fuel cells but also in solid electrochromic devices (Vyas et al. 1986).

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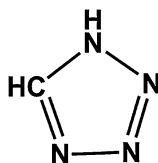
Texture Recognition

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Tetrazole Group,

Fig. 1 Chemical structure of tetrazole



There are a variety of methods used to determine the porosity of a membrane, such as mercury porosimetry, microscopy, physisorption, etc. (Mulder 1996; Palacio 1999). And from them, the method that provides more information about

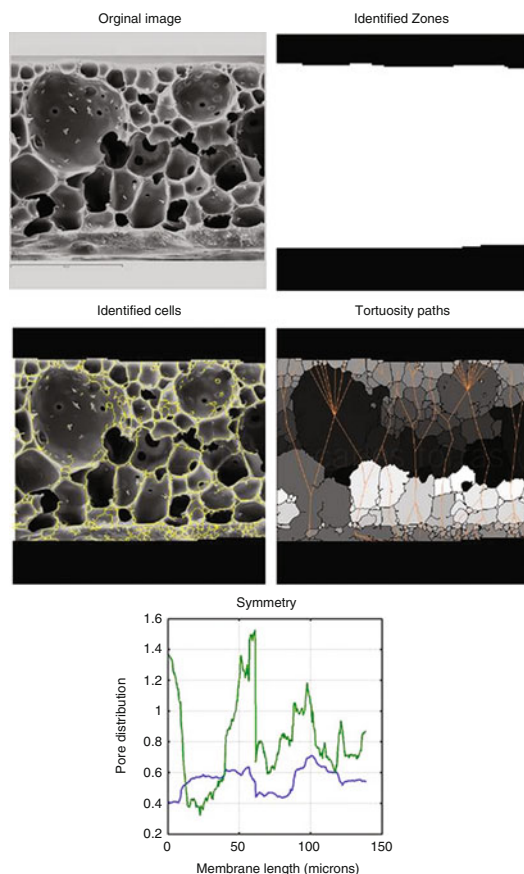
the whole porous structure of a membrane is, probably, scanning electron microscopy (SEM) by obtaining surface and cross-section membrane micrographs (Kools 1998). Often, the pore size, shape, etc. of a membrane are different depending on the position and caused by the process of membrane formation. These variations are considered through several morphological parameters such as regularity, symmetry, etc. (Torras and Garcia-Valls 2004). They imply significant effects to the membrane performance (Torras et al. 2006).

But an inconvenient of SEM technique is that it provides only qualitative results through micrographs (Torras and Garcia-Valls 2004). Thus, it is necessary to interpret the images numerically for a variety of reasons: obtain correlations between membrane morphology and synthesis conditions, between membrane morphology and membrane performance, etc. This can be achieved by modeling the porous structure. There are some methodologies to achieve it, such as fractals (Tam and Tremblay 1993), phase field simulation (Zhou and Powell 2006), or molecular simulation approaches (Chang et al. 2010). Recently texture recognition has also been tested for this purpose with promising results and from SEM membrane micrographs (QUANTS methodology – software) (Torras et al. 2011).

Texture recognition is a field of knowledge proper from computer vision. Texture is a visual sign used in a wide number of computer vision tasks because it allows differentiation between objects or surfaces that appear in the image and have a similar shape or color (Bernard-Michel et al. 2002; Lin and Miller 2000). Unfortunately, texture is one of the signs that are most difficult to model because it is intrinsically noisy by nature, and it is affected by different external factors such as illumination, rotation, or scale, which alter its perception. This complexity has caused an intense research during the last decades (Haralick 1979; Manjunath and Ma 1996; Randen and Husoy 1999), which has allowed the publication of a large number of methods to represent texture. Texture can be visualized within structural patterns of surfaces of natural or artificial objects such as wood, sand, grass, textiles, or skin and measured through surface properties such as roughness, regularity, etc.

By applying texture recognition methodologies with membrane micrographs obtained from SEM (Gabor wavelets, watershed transformation, etc.), it is possible to detect and identify the pores that are present in a micrograph, without user intervention. The result is that an artificial image (a simile of the micrograph) can be obtained and computation of several parameters can be performed, such as number of pores, distribution, porosity, changes of pore size along each direction (and consequently, computation of parameters such as regularity or symmetry), tortuosity, etc. (Torras et al. 2011). The only and main limitation of the method is the resolution of the micrograph (Fig. 1).

In conclusion, a main advantage of applying texture recognition techniques over membrane



Texture Recognition, Fig. 1 Original cross-section membrane micrograph obtained by SEM and results achieved after interpreting the original image with QUANTS software (only showing graphical results)

micrographs is that numerical results of its morphological properties can be obtained in a systematic, reliable, quick, and non-expensive way.

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Thermally Induced Phase Separation (TIPS) for Membrane Preparation

Alberto Figoli

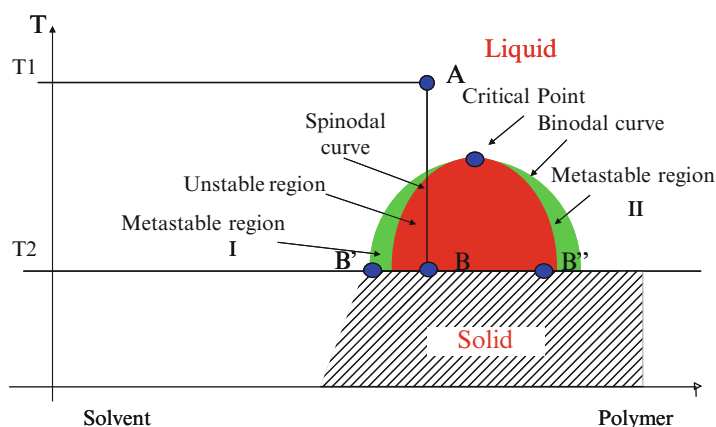
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Phase Inversion (PI) or Phase Separation (PS) is one of the most diffused and versatile methods for preparing polymeric membranes. It is based on the precipitation/solidification of a polymer-rich phase from an initially homogenous system, the casting solution, containing the polymer (P), properly dissolvent in an appropriate substance, named solvent (S) or diluent (D). The thermodynamic basis of phase separation is the existence of a miscibility gap in the P/S system, i.e., an ensemble of conditions such that the polymer is not soluble anymore and starts to precipitate and demix from the solution. There are different methods to induce phase separation; in thermally induced phase separation, or TIPS, polymer precipitation is caused by a decrease of temperature, normally provoked by immersion in a quenching bath. Membrane preparation via TIPS requires the finding of an appropriate diluent or “latent solvent,” i.e., a substance that is not able to dissolve the polymer at room temperature but that behaves as a solvent at temperature close to the polymer melting point. Once obtained a homogeneous system, the solution is cast or extruded to obtain a flat sheet or a hollow fiber membrane; temperature decrease induces phase inversion. Then, it is normally necessary to exchange the polymer diluent with a more volatile substance, as an alcohol, for removing it; finally, the membrane can be dried.

The phenomenological description of TIPS can be done with the aid of binary phase diagrams (Strathmann et al. 2010), which show the boundaries of the stable, metastable, and unstable P/S compositions as a function of temperature. The spinodal curve delimits the unstable region, while the metastable region is enclosed between the spinodal and the binodal curves. When the temperature T_I of a generic homogeneous solution

Thermally Induced Phase Separation (TIPS)

for Membrane Preparation,
Fig. 1 Binary phase diagram describing TIPS



decreases from a point located in the stable region (Point A, Fig. 1) to a point located in the miscibility gap (Point B at T₂), below the spinodal curve, phase separation takes place. The system will separate in two phases (B' and B''), corresponding to the polymer-rich and the polymer-lean phases; they will give rise to the membrane and its pores, respectively.

Membrane formation can take place, in general, via liquid-liquid (L-L) or solid-liquid (S-L) demixing; this depends on several factors, as polymer type and concentration and diluent type. Furthermore, other phenomena as vitrification and gelation may occur.

In L-L demixing, after the system crosses the binodal curve, either spinodal decomposition (SD) or nucleation and growth (NG) can proceed. NG can occur only in the metastable region between the binodal and the spinodal curves; two cases can be distinguished. If phase separation proceeds via NG of the polymer-rich phase in the solvent phase (Metastable region I, in Fig. 1), a structure with poor integrity is obtained. NG of polymer-lean phase in the solid polymer-rich matrix usually gives rise to isolated pores (Metastable region II, in Fig. 1). SD happens when the systems enter directly in the miscibility gap (usually via a sudden cooling) and may result in bicontinuous structures with high interconnectivity. S-L demixing can be observed only for crystalline and semicrystalline polymers, if the polymer crystallization temperature is reached during cooling. Chain-folded lamellae and supramolecular architectures, as axialites and spherulites, can be observed in this case.

TIPS can be applied to prepare membranes from polymers that are difficult to dissolve at room temperature in common organic solvents, as polypropylene. Furthermore, TIPS has been reported as an alternative method for preparing membranes from more soluble polymers, as PVDF, which can be used also in other techniques as non-solvent-induced phase inversion.

Cross-References

► [Melt Spinning](#)

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Thermopervaporation (Thermo-PV)

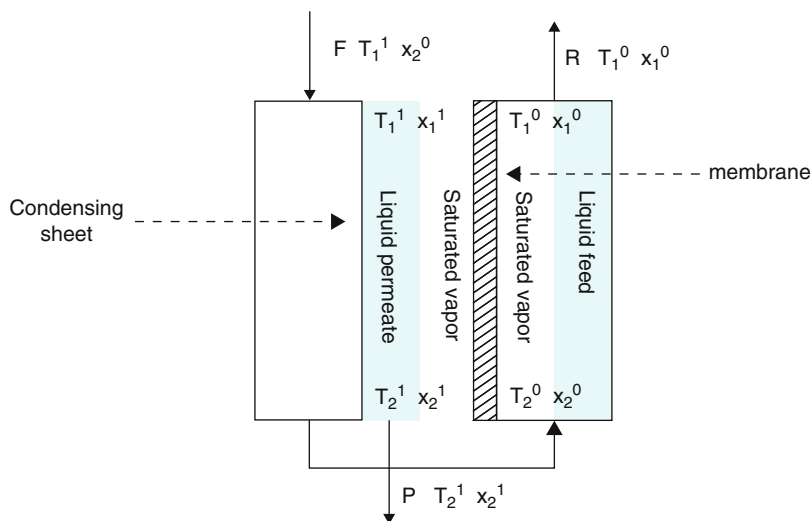
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Pervaporation is a membrane separation process which is based on difference of vapor pressure as driving force. It is a well-established tool for

Thermopervaporation (Thermo-PV),

Fig. 1 Concept of thermopervaporation (Eva et al. 2010)



component recovery from the aqueous phase. Nowadays, pervaporation is usually performed industrially with vacuum as driving force. Vacuum pumps are switched periodically to remove non-condensable gases. For some actual production process, it is unfavorable (Volkov and Bortisov 2012). In vacuum operation only a small pressure loss can be allowed at the permeate side, because an increase in partial downstream pressure influences flux and selectivity negatively. Since large apparatus volumes are necessary, leakage problems may occur, oxygen might diffuse into the apparatus, which would lead to oxidation (Franken et al. 1990).

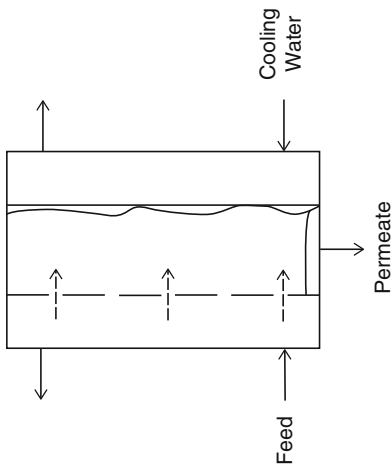
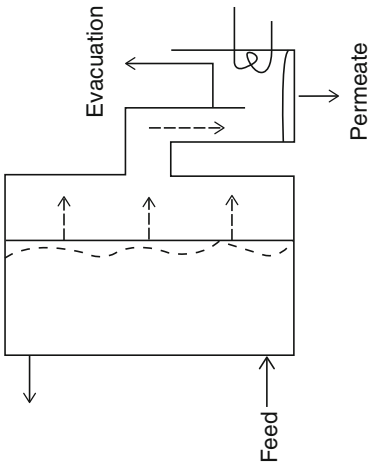
Thermopervaporation is also called thermopervaporation or thermo-PV. It overcomes the drawbacks of vacuum pervaporation. A reduced partial pressure at the permeate side can also be gained by a temperature difference between feed side and permeate side of the membrane. Based on this technology, it is possible to integrate the condensation energy for direct heating of the feed during pervaporation in one single module. Thermopervaporation is a new concept for pervaporation that benefits from small distances in a membrane module to recover internal heat to the most.

The thermopervaporation process (shown in Fig. 1) aims at making effective use of the

condensation energy of pervaporation vapors. The energy comes from heating the feed. Shortening the vapor transport distances can make the most use of the energy. The initial feed stream (F) enters the module in the condenser at temperature T_1^1 (heat resistance in the condenser has been neglected). The feed is heated up to T_2^1 using enthalpy of condensation of the permeate (P). Then the feed temperature is further increased to T_2^0 by means of an external heat source. There are resulting vapor pressure differences between feed and permeate side of the membrane, so a fraction of the feed permeates the membrane as a vapor and condenses on the condenser plate (Eva et al. 2010). There are many differences between thermopervaporation and pervaporation, which are shown in Table 1.

With the thermopervaporation concept, it is possible to recover heat during pervaporation process in an efficient manner. The process has been established using ethanol separation. Thermo-PV can be operated using low-cost heat (80–100 °C), which is effective in actual production. Besides, the experiments were carried out in a small and suboptimally configured module; results showed that this concept has great potential for commercial applications (Eva et al. 2010).

Thermopervaporation (Thermo-PV), Table 1 Features of thermopervaporation in contrast with pervaporation (Nitta et al. 1986)

Principle	Model	Thermopervaporation	Pervaporation
			
Membrane	Mechanism	Evaporation to permeation	Permeation to evaporation
	Driving force	Temperature (steam pressure) difference	Pressure difference
	Material	Hydrophobic	Hydrophilic
	Structure	Porous	Nonporous
Operation pressure		Normal pressure	Evacuation
Operation temperature		Less than boiling point	Room temperature

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Thermoresponsive Membrane Surfaces

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Thermo-responsive membrane surfaces (also called thermosensitive membrane surfaces) are membranes with thermo-responsive/thermo-sensitive surfaces prepared by grafting or coating thermo-responsive/thermo-sensitive materials onto the membrane surface by certain chemical or physical methods. The substrate membranes provide mechanical strength and dimensional stability, while the conformational changes of the grafted thermo-responsive polymers on the membrane surfaces result in the thermo-responsive characteristics. The surface wettability characteristics and the membrane resistance as well as transmembrane permeability of such membranes can be controlled or adjusted by self-regulation according to the responsive conformational change of the grafted or coated thermo-responsive materials on the membrane surfaces. Because there are numerous cases in which environmental temperature fluctuations occur naturally, and the environmental temperature stimuli can be easily designed and artificially controlled, much attention has been focused on thermo-responsive

membrane surfaces. Such membranes can be used for both controlled release and advanced separation by utilizing the thermo-responsive conformational change of the functional surface layer (Chu 2011).

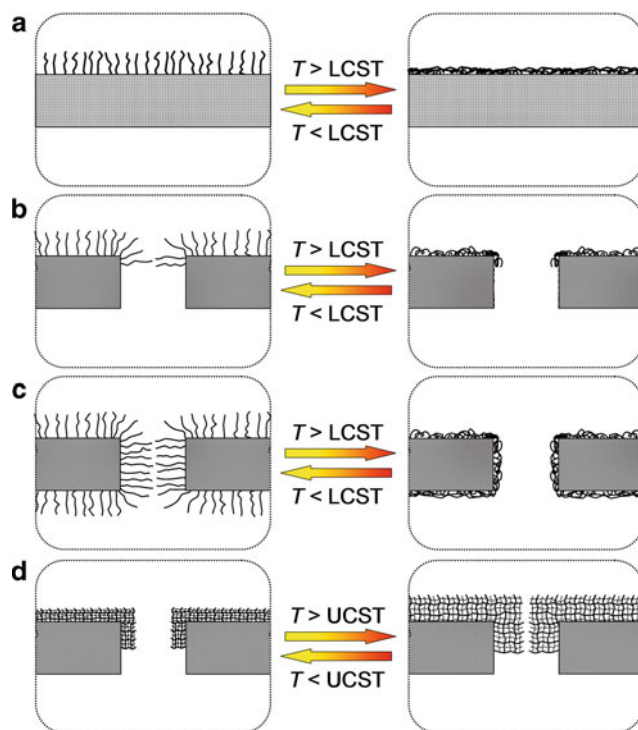
Various grafting techniques, including chemical grafting, plasma-induced grafting, radiation-induced grafting, and so on, can be employed to prepare thermo-responsive membrane surfaces by grafting thermo-responsive polymers onto the membrane surfaces. According to the location of grafted polymers on the membranes, thermo-responsive membrane surfaces can be classified as surface-covering model (Fig. 1a), pore-covering model (Fig. 1b, d), and pore-filling model (Fig. 1c) (Chu et al. 2011). For the pore-covering and pore-filling models (Fig. 1b–d), the effective membrane pore sizes can be self-regulatively adjusted by the thermo-responsive volume phase transition behaviors of the grafted thermo-responsive materials, i.e., the grafted thermo-responsive materials can act as smart valves that respond to environmental temperature stimuli.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a popular thermo-responsive polymer. It shows a distinct and reversible phase transition at the lower critical solution temperature (LCST) around 32 °C. PNIPAM-based polymers are usually used to fabricate thermo-responsive membrane surfaces (Fig. 1a–c). When the environmental temperature is lower than the LCST, the PNIPAM-based materials exhibit a swollen and hydrophilic state; however, when the temperature is higher than the LCST, the PNIPAM-based materials show a shrunken and hydrophobic state. By such thermo-responsive conformational change of the membrane surface layer, the surface wettability characteristics and the membrane resistance as well as transmembrane permeability of the membranes can be self-regulatively controlled or adjusted according to the environmental temperature change (Chu 2011).

Interpenetrating polymer networks (IPNs) of poly(acrylamide) (PAAM) and poly(acrylic acid) (PAAC) are featured with a thermo-responsive volume phase transition characteristic that is the reverse of that of PNIPAM, i.e., the swelling of PAAM/PAAC-based IPNs is induced by an

Thermoresponsive Membrane Surfaces,

Fig. 1 Schematic illustration of thermo-responsive membrane surfaces grafted with responsive materials possessing thermo-induced shrinking (a–c) and thermo-induced swelling behaviors (d). (a) Surface-covering model, (b, d) pore-covering model, and (c) pore-filling model



increase rather than a decrease in temperature. Therefore, the thermo-responsive membrane surfaces constructed from PAAM/PAAC-based IPNs are featured with negatively thermo-responsive characteristics (Fig. 1d) (Chu et al. 2005). When the environmental temperature is lower than the upper critical solution temperature (UCST) of the PAAM/PAAC-based IPN gel, the IPN hydrogels retain a shrinking state. On the other hand, when the environmental temperature is higher than the UCST of the IPN gel, the IPN hydrogels retain a swelling state. For the pore-covering model (Fig. 1d), the effective membrane pores change from an “open” situation into a “closed” situation when the temperature increases from one that is below the UCST to another that is above the UCST.

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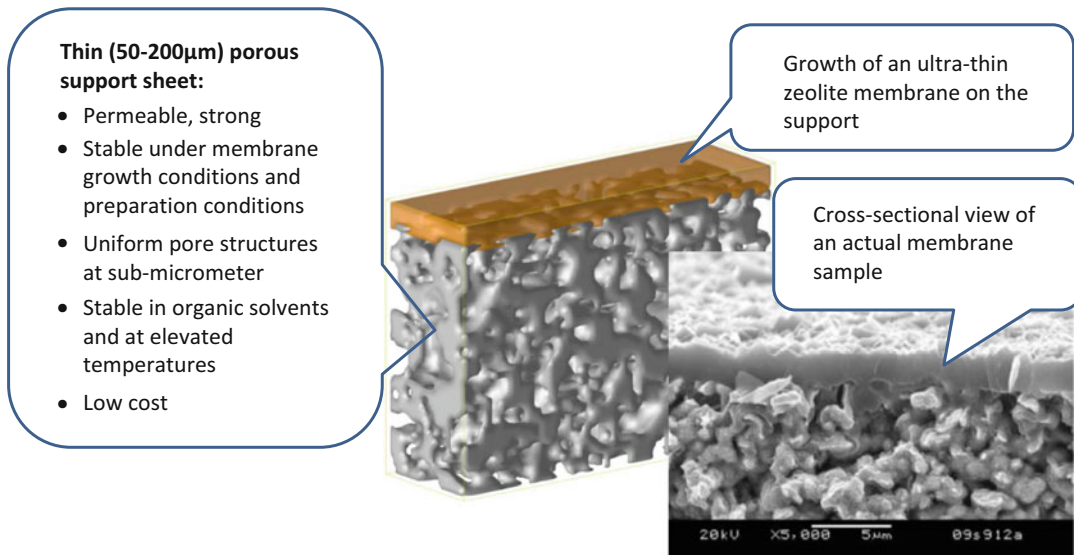
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Thin-Sheet Zeolite Membranes

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Zeolite materials possess some unique properties, such as molecular-sieving functions, excellent chemical and thermal stability, and low costs. Today, zeolites are used in a variety of catalytic reaction and adsorption separation processes. They are a very attractive class of materials for membrane usage. A large number of scientific articles and patent applications have been published on zeolite membranes for recent two



Thin-Sheet Zeolite Membranes, Fig. 1 Design concept of thin-sheet zeolite membranes

decades. The feasibility of making zeolite membranes and their unique molecular-sieving functions was demonstrated in the late 1990s and early 2000s, which includes those common zeolite frameworks consisting of SiO_2 , Al_2O_3 , and Na_2O , such as NaA, X-type, Y-type, ZSM-5, silicalite, and mordenite. For example, the flux and selectivity of a zeolite membrane was reported to be one to two orders of magnitude higher than the polymeric membranes for solvent dehydration (Morigami et al. 2001).

Zeolites are ceramic-type materials, and self-supported zeolite membranes are too fragile to be made as large sheets (or plates). Thus, zeolite membranes are typically grown on a porous support structure. Ceramic disks and tubes have been used in most literature studies so far. Occasionally, sintered metal tubes and frits were used. Those supporting materials serve well for the purposes of fundamental studies and proof of concept experiments. For actual membrane product development, however, novel product designs and manufacturing processes are needed to produce large zeolite membrane areas suitable for industrial applications at a cost competitive with existing separation technologies.

Ceramic tube-supported zeolite membranes are now commercially available. These tubes have a

length about 1 m and outer diameter from 1.0 to 3.0 cm. A number of membrane tubes can be bundled together to form a membrane module or separation device. Those zeolite membranes are demonstrated at pilot and small-scale commercial plants for dehydration of alcohols and organic solvents. However, their cost (Caro and Noack 2009), which ranged from \$1,000 to 3,000/ m^2 , is too high to be used widely. In addition, a great number of membrane tubes are required for large-scale industrial processes, which present significant challenges to engineering and installation of membrane separation equipment. For example, it is estimated that about 70,000 of membrane tubes are needed for ethanol dehydration in a medium-size ethanol plant of 150 million liters per year production capacity. Instead of a single hole, several holes are made into one membrane tube to achieve incremental improvement to the membrane area packing density.

One approach to address the cost and membrane area problems is to make zeolite membranes like polymeric membrane sheets. Spiral wound polymeric membranes are made at fairly low costs and used in large-scale seawater desalination. The design concept of thin-sheet zeolite membranes is illustrated in Fig. 1. One critical challenge is the support structure. Thinness of

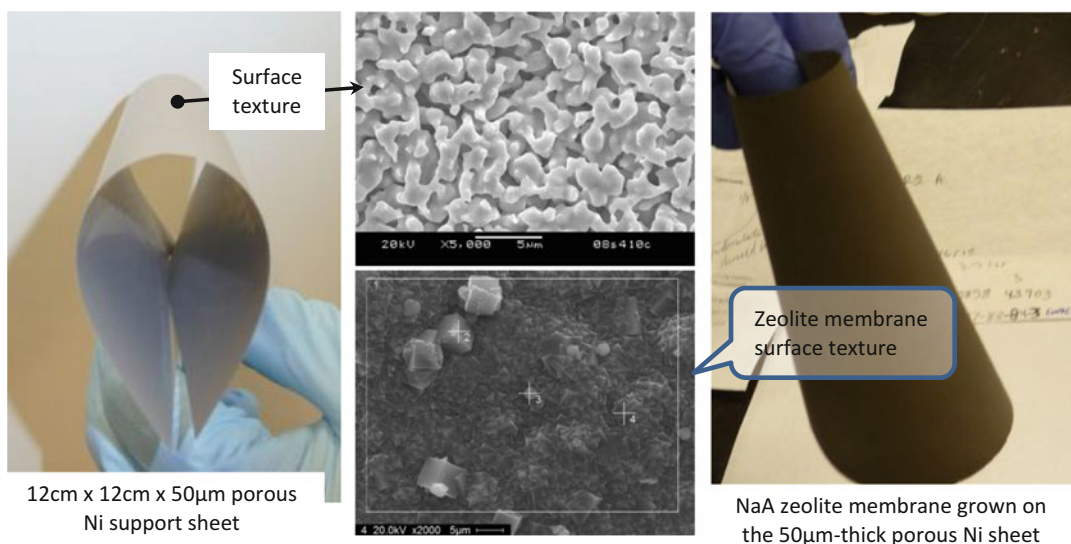
the support sheet is necessary to reduce material consumption, membrane weight, and transport resistance. Thin sheets also enable package of large membrane areas in a given volume, i.e., obtaining high membrane area packing density.

As general requirements of a membrane support, the support sheet needs to be highly permeable so that mass transport through the support would not present a significant resistance for most separation applications, and the support sheet needs to be sufficiently strong to provide the mechanical strength for the membrane sheet to withstand a pressure gradient under separation conditions for a long time. The specific requirements pertinent to zeolite membrane preparation are (i) stability under zeolite membrane growth and preparation conditions, (ii) uniform surface pore structures at micro- and sub-micrometer levels, and (iii) stability under the zeolite membrane separation conditions. The growth of a zeolite membrane typically occurs in a strong basic solution at temperatures ranging from 60 °C to 180 °C. After growth, posttreatment sometimes is needed for the removal of templates and opening of zeolite pores. The possible post-treatment methods are oxidation in an O₂ gas environment at high temperatures, oxidation in plasma or ozone gas environment at moderate or low temperatures, and solvent extraction. Having a uniform surface pore structure at micro- and sub-micrometer levels is necessary for deposition of a thin, continuous zeolite membrane layer on the support. It is obvious that a continuous zeolite membrane less than 10 μm thick cannot be formed on a support surface of pores or defects larger than 10 μm. The zeolite membrane can work under separation conditions that could be problematic to polymeric materials, such as in hydrocarbon and organic solvent media and at high temperatures (relative to environment). Thus, the support sheet needs to be stable under separation conditions so that application and performances of the zeolite membrane would not be compromised by the support. Finally, the support sheet needs to be low costs.

No commercially available materials could be found yet when the above criteria were applied to the selection of a suitable support sheet. Porous

ceramic disks work well as a zeolite membrane support but have not been made as thin, strong, inexpensive sheets yet. Sintered metal plates meet the requirements of mechanical strength and chemical and thermal stability. But they are too thick and too expensive. On the other hand, metal foams and metal meshes have the pore opening too large to be deposited with a thin, continuous zeolite membrane layer. Micro- and ultrafiltration polymeric membranes have adequate surface pore structures but fall short of chemical and thermal stability. No report on formation of high-performance zeolite membranes on a polymeric support has been found yet.

Thin porous metallic sheets have recently been developed that can meet all the above criteria (Liu et al. 2011a; Liu and Canfield 2012). The thin-metal sheets made of Ni, Ni alloys, and steels possess the physical and chemical properties of those metallic materials and provide suitable pore structures for the preparation of a thin layer of zeolite membranes. These metal sheets are made of inexpensive metal oxide raw materials and have large potential for mass production at low costs. As a reference, steel sheets and plates are produced at a price as low as \$1/kg. It was demonstrated that zeolite membranes can be directly prepared on such supports by secondary growth methods (Liu et al. 2011b). The secondary growth consists of two basic process steps: seeding and growth. The support surface is first coated with a layer of small crystals of targeted zeolite framework that act as a seed for zeolite crystal growth. The seed coating also helps smoothening of the support surface. Then, a continuous layer of intergrown zeolite crystals is formed by hydrothermal growth of the seeded support under suitable conditions. Thin-sheet zeolite membranes grown on such a support are illustrated with a NaA membrane in Fig. 2. The 50 μm-thick porous Ni alloy sheet is strong enough to be self-supported and flexible enough to bend and shows uniform surface pore structures. After membrane growth, the sheet surface changes its color from metallic gray to darken glassy luster. A dense and continuous membrane layer comprising intergrown zeolite crystals is formed on the metallic support surface. No cracks and pinholes



Thin-Sheet Zeolite Membranes, Fig. 2 NaA zeolite membrane grown on 50 μm -thick porous Ni sheet support

are seen. Although there are different sizes and shapes of crystals on the membrane, a pure NaA crystal phase is confirmed by X-ray diffraction analysis. It is worth noting that the zeolite membrane shows excellent adhesion onto the support, which is largely attributed to the thinness of the zeolite membrane layer. The zeolite membrane is so thin that the membrane-grown sheet behaves similar to the bare metal sheet, strong and flexible.

The thin-sheet design paves the way for mass production of zeolite membranes at competitive cost. Materials used to make the metal sheet support and prepare zeolite membranes are typically inexpensive commodity products. By making thin-sheet membranes, the raw materials become a minor cost factor. The membrane cost will be largely determined by the preparation process costs. Current planar sheet or plate products, such as papers, metal foils, glass, and polymeric membranes, are manufactured in large bulk quantities at fairly low costs. It is expected that the thin-sheet zeolite membrane can be mass produced by utilizing automated, high-throughput sheet-to-sheet-type manufacturing processes.

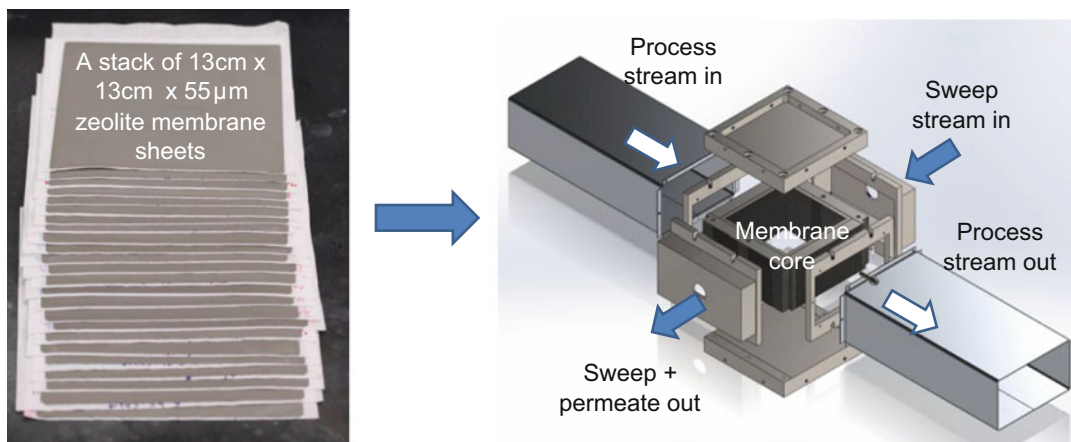
The thin sheet enables fabrication of membrane modules or membrane separation

equipment with maximum membrane area and/or minimal mass transfer resistance from bulk to membrane surface. A cross-flow planar module (Fig. 3) is used to illustrate the making of a separation device with the thin-sheet zeolite membrane. An array of membrane sheets is packaged together to form respective feed and permeate channels by the use of proper backing and spacing materials. The sweep (or permeate) and feed (or process) streams are separated by the membrane sheet and flow in perpendicular directions. The membrane surface per unit volume (SA_V) of the stack for this module design can be estimated by the following equation:

$$SA_V = \frac{1}{0.5L_p + 0.5L_F + L_m}$$

where L_p , L_F , and L_m are permeate (or sweep) channel spacing, feed (or process) channel spacing, and membrane thickness, respectively. If $L_p = 1 \text{ mm}$, $L_F = 1 \text{ mm}$, and $L_m = 0.05 \text{ mm}$, SA_V can be $952 \text{ m}^2/\text{m}^3$. Using small channel spacing reduces the mass transfer resistance from bulk to membrane surfaces and increases the membrane area packing density.

In summary, zeolite membranes supported on a thin porous metal sheet are compared to other



Thin-Sheet Zeolite Membranes, Fig. 3 Package of thin membrane sheets into a working module for cross-flow separation and mass transfer

Thin-Sheet Zeolite Membranes, Table 1 Comparison of thin-sheet zeolite membranes to other membrane products

Material	Application	Cost	Characteristics
Polymer	Various commercial products from microfiltration, ultrafiltration, and nanofiltration to molecular separation	Fair	Working well in water medium at ambient or room temperatures
Hollow fiber			
Sheet	~\$10 billion/year global market		Stability issues at high temperatures and in organic solvents or oil
Ceramic	Some specialized applications	High	Tolerance to organics
Tube	A few hundred million \$/year market		Excellent thermal stability
Monolith			Fragile
Metal	Some specialized applications with limited market penetration	High	Ductile and strong
Tube			Tolerant to organics
Thin-sheet zeolite/metal membrane	Porous metal sheet as micro- and ultrafiltration membrane	Fair	Fair thermal stability
	Zeolite membranes for a number of important molecular separation processes		Advantages of metal and zeolite materials
			Module package like polymeric sheets

membrane materials and products in Table 1. This hybrid membrane technology is expected to preserve unique properties possessed by the zeolite and metallic materials and eliminate their shortcomings at the same time. Thus, the hybrid thin-sheet membrane can provide performance and cost advantages that are not achievable using individual materials alone. There is a great opportunity to further develop this membrane technology for various applications and to expand the design concept to other material systems.

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3D-Imaging Methods for Membranes

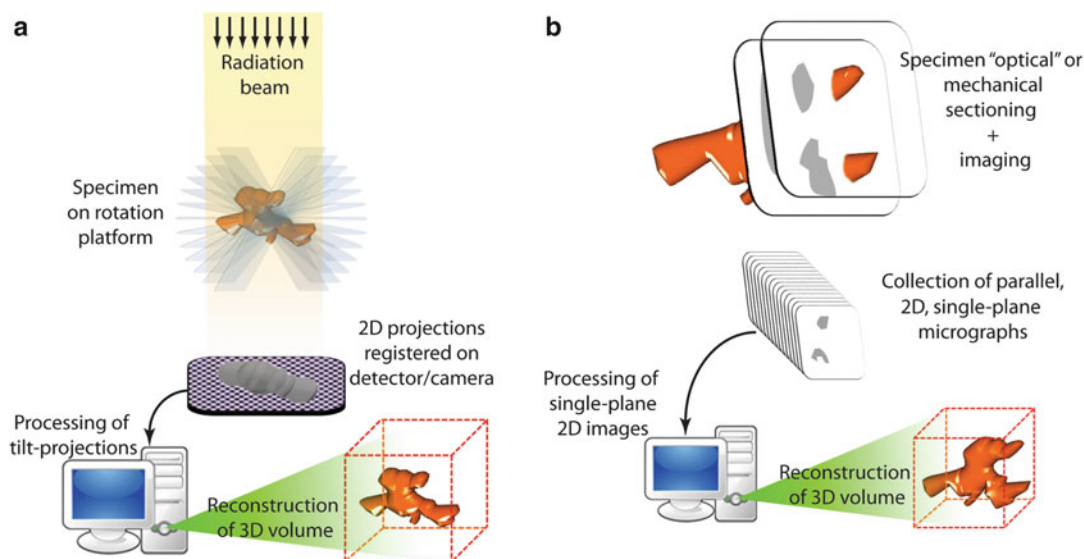
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Synonyms

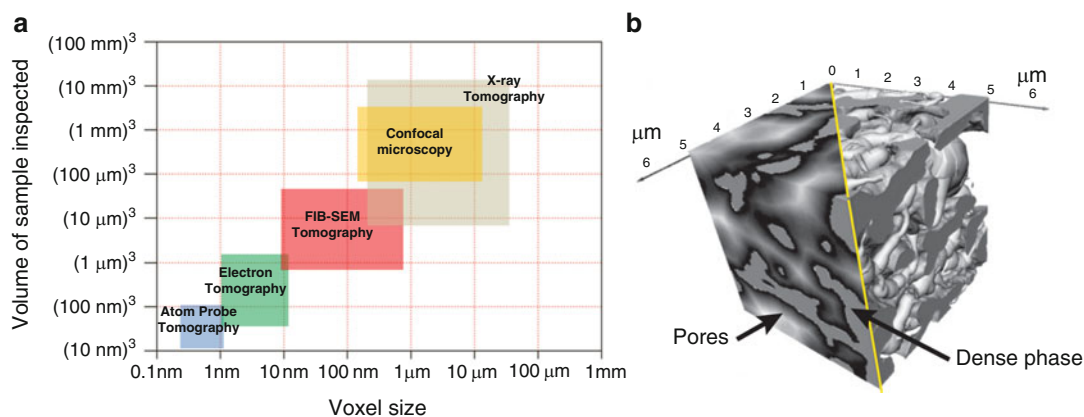
Three-dimensional (3D) microscopy methods;
Tomographic microscopy methods

Three-dimensional (3D) microscopy methods (also known as tomographic microscopy methods) (Van Tendeloo et al. 2012) are imaging techniques which provide three-dimensional visualization of the internal structure of solid materials. They are employed to investigate the inner architecture of a wide range of membranes. *Tomography*, from Ancient Greek terms *tomos*

(slice) and *grapho* (to write, to record), refers to the possibility of mapping internal sections of the studied object and thereby reconstructing its 3D structure. Most tomographic methods, e.g., those discussed in this entry except from *Atom-probe tomography*, can be divided into two main groups depending on their working principle. Some methods rely on recording a series of two-dimensional (2D) projection images of the sample under different observation angles. Other tomographic techniques rely on the acquisition of sectional views of several, generally parallel, internal planes of the material. Figure 1 depicts schematic representations of the working principle of tomographic imaging methods based on projection (Fig. 1a) and sectional (Fig. 1b) 2D images (*micrographs*). While projection-based methods are nondestructive, i.e., the sample specimen is preserved, some section-based methods are destructive as they rely on mechanical slicing or erosion of thin layers of the material being imaged. The collection of two-dimensional *micrographs*, either projections or single-plane sectional views, is then aligned, often with the help of fiducial markers added onto or next to the sample specimen, and processed with dedicated mathematical algorithms (Herman and



3D-Imaging Methods for Membranes, Fig. 1 Schematic representation of the working principle of tomographic imaging methods based on (a) projectional 2D views and (b) inner-sectional 2D views



3D-Imaging Methods for Membranes, Fig. 2 (a) Plot representing the typical ranges of voxel size and volume of sample inspected in a single experiment for several tomographic imaging methods (Adapted from Uchic et al. 2007); (b) surface-rendered 3D view of a

reconstructed X-ray computed tomogram of a microfiltration membrane (Adapted from Reingruber et al. 2011). *Left side* shows a distance map, and *right side* a tube-type representation of the membrane porosity

Joachim 2014) to reconstruct the internal structure of the solid sample in three dimensions. Such reconstruction is named *tomogram*.

In the following, selected tomographic imaging methods of particular interest to investigate membranes are defined. For these methods, Fig. 2a indicates characteristic ranges for the size of the voxels, i.e., the most elemental unit in a tomogram (equivalent to a pixel in a 2D image), as well as for the volume of sample which can typically be examined in a single experiment. As observed there, the highest is the resolution of the method, i.e., the smaller is the voxel size, the higher is the local character of the technique, i.e., the more limited is the volume of material from which information can be gathered in a single experiment.

Atom-probe tomography (APT) is a 3D-imaging method with atomic resolution and elemental sensitivity, i.e., it does provide information about the chemical composition of the sample studied. Unlike the rest of the tomographic methods considered in this entry, the imaging principle of APT does not involve manipulation of radiation. Experimentally, the sample specimens must be shaped in the form of a sharp tip. The specimen is then exposed to strong electric field pulses which are capable of overcoming the atom-bonding forces in the solid, causing ionization and vaporization of atoms from the surface

of the sample. APT is therefore a destructive imaging method. The emitted ions are subsequently accelerated in the electric field and projected onto a position-sensitive detector which identifies the nature of each detected ion by its time-of-flight from the surface of the specimen to the detector (related to the charge-to-mass ratio of the ion) and reconstructs its position in the original specimen from its point of impact on the detector surface. Through successive evaporation of several layers of atoms from the sample surface, the method allows reconstructing a 3D view of the processed sample, providing atomic scale and elemental information on its structure.

Electron tomography (Frank 2008), also known as 3D transmission electron microscopy (3DTEM), is the three-dimensional version of transmission electron microscopy (TEM). This is a representative projection-based, nondestructive imaging method. Experimentally, a collection of 2D projections (*micrographs*) of the sample is recorded upon tilting the specimen in the transmission electron microscope in a range of angles along either a single or more rotation axis. In the classical version of the method (bright-field ET), each projection image is generated by recording the attenuation of electrons as a function of the position within the illuminated sample specimen. Alternative imaging methods involve rastering the

sample with an electron beam and recording electrons, not transmitted through, but scattered from the specimen at high angles (tomographic high-angle annular dark-field scanning transmission electron microscopy, HAADF-STEM) (Pennycook and Nellist 2011). Features down to the nanometer, in some instances even atomic, scale can be imaged for thin sample specimens, typically less than 400 nm thick in the direction of the illumination beam.

FIB-SEM tomography, also known as tomographic FIB-SEM, is exemplary of sectional-based, destructive imaging methods. To be imaged, the solid specimen is previously spattered with metal overlays to increase sample conductivity. A trench is first carved on the upper surface of the sample with a focused ion beam (FIB). Also the FIB is used later to remove thin parallel layers of material, exposing cross sections of the internal structure of the specimen which are consecutively imaged with a scanning electron microscope (SEM). The resulting stack of SEM *micrographs* of parallel internal planes of the sample is then aligned and processed to reconstruct the internal structure of the volume of sample processed with the FIB. Typically sample volumes in the range of 1–50 μm^3 can be studied in a single experiment, with 3D-imaging resolutions down to 10–30 nm, being the limiting factor of the resolution of the FIB-milling process.

X-ray tomographic microscopy (XTM), also known as X-ray microcomputed tomography (μCT) (Stock 2009), is based on recording a collection of 2D projections of the sample specimen. Similar to the case of ET, each projection image is generated by recording the attenuation of, in this case, X-rays as a function of the position within the illuminated sample specimen. The collection of projections is recorded typically via precise rotation of the sample while keeping the X-ray source and detector stationary. The highest spatial resolution, down to sub-micrometer levels, is achieved with high-intensity X-ray sources in synchrotron facilities.

Confocal scanning microscopy (CSM) (Paddock 1999) is an optical imaging method, hence based on the detection of photons. In contrast to conventional optical microscopes, in

confocal optical microscopes, the sample is illuminated by a single point of light, generally from a laser source, and a pinhole is located in front of the detector allowing the detection of exclusively “in-focus” light originating via, e.g., a fluorescence process from a selected internal plane of the sample. Sequential imaging of several internal planes, at different heights along the sample, allows the 3D reconstruction of its internal structure. Such “optical sectioning” approach could be regarded as a nondestructive analog of the working principle of FIB-SEM tomography.

Most of these tomographic microscopy methods have recently become important diagnostic tools in the design and assembly of a wide array of technological membranes. The suitability of each tomographic method to investigate different structural features in modern membranes is closely linked to their inherent spatial resolution.

The chemically sensitive, atomic-scale information offered by APT makes it suitable to study grain boundary compositions and phase segregation phenomena in dense ceramic or alloy-type membranes. ET permits visualization of nanometer-sized objects within a continuous matrix and has been applied to investigate the internal structure of membranes based on microporous silica doped with metal nanoparticles, which find application in high-temperature hydrogen separation processes (Yoshida et al. 2009). FIB-SEM tomography, with a 3D resolution down to few tens of nanometers, allows three-dimensional visualization of the most common membrane defects such as pinholes, cracks, or voids. For membranes incorporating nanometer- or micrometer-sized filler materials within a continuous matrix, e.g., *mixed matrix membranes*, FIB-SEM tomography enables assessing the local concentration, three-dimensional spatial location, and orientation of the filler components (Rodenas et al. 2014). The resolution provided by XTM, in the micrometer range, permits imaging the porosity of, e.g., microfiltration membranes. The three-dimensional membrane models resulting from the reconstructed tomograms (see Fig. 2b for an illustration) can be used as the basis to simulate fluid permeation through the membrane. In the case of CSM, the sub-micrometer

spatial resolution, in combination with the selective imaging of, e.g., fluorescent species, makes it suitable to study the three-dimensional spatial distribution of biomolecules and other structures, either intrinsically fluorescent or adequately stained with a fluorescent contrast agent, within the porous structure of microfiltration. This approach has been demonstrated to investigate the process of membrane (bio-)fouling (Zator et al. 2007).

Cross-References

- [FIB-SEM Tomography](#)
- [Membrane Fouling](#)
- [Membrane Micrograph](#)
- [Mixed Matrix Membranes \(MMMs\)](#)

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Three-Dimensional (3D) Microscopy Methods

► 3D-Imaging Methods for Membranes

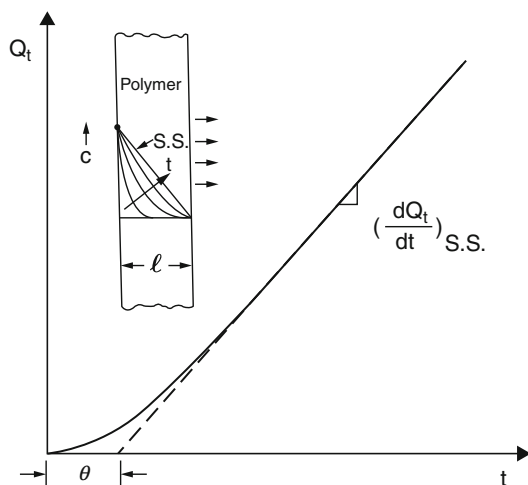
Time Lag Method for Mass Transport Properties Evaluation in GS

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The diffusion time lag method is a useful way to obtain the diffusion, solubility, and permeability coefficients from a single experiment when certain conditions are satisfied. It takes advantage of the initial transient portion of a permeation experiment prior to the establishment of steady-state permeation. Considering a polymer membrane of thickness l with an initial concentration of penetrant of C_0 throughout and at time $t = 0$, the concentration of penetrant is set at C_2 within the upstream face of the membrane and C_1 at the downstream face. The accumulative amount of penetrant per unit area exiting the downstream surface of the membrane, Q_t , versus time can be obtained from a solution to Fick's second law when the diffusion coefficient is constant (independent of concentration and position in the membrane), and there are no chemical reactions or adsorption processes (Crank 1975). The result is

$$Q_t = D(C_2 - C_1)t/l + \frac{2l}{\pi^2} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n^2} \{1 - \exp(-Dn^2\pi^2 t/l^2)\} + \frac{4C_0 l}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \{1 - \exp(-D(2m+1)^2\pi^2 t/l^2)\} \quad (1)$$



Time Lag Method for Mass Transport Properties Evaluation in GS, Fig. 1 A transient permeation experiment illustrating the time lag and the steady-state region (Paul 2010) (Reproduced with permission by Elsevier (Copyright 2010))

The most common situation is when $C_1 = C_0 = 0$ for which Eq. 1 simplifies to

$$Q_1 = lC_2 \left[Dt/l^2 - 1/6 - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp(-Dn^2\pi^2 t/l^2) \right] \quad (2)$$

At long enough times, the exponential terms vanish, and Eq. 2 approaches the linear asymptotic line given by

$$Q_1 = \frac{DC_2}{l} [t - l^2/6D] \quad (3)$$

This steady-state line intercepts the time axis at $t = q$ or the “time lag” given by

$$\theta = l^2/6D \quad (4)$$

as illustrated in Fig. 1. The full solution for Q_1 , Eq. 2, becomes experimentally indistinguishable from the asymptotic line for $t^3 \gg 3q$. A common error in using this method is not allowing enough time to establish steady state.

For simple gases, the equilibrium concentration of gas in the polymer, C , for a given external

pressure p is given by Henry’s law, $C = Sp$, where S is a solubility coefficient. The permeability coefficient P can be calculated from the slope of the steady-state portion of the graph of Q_1 versus t by the definition

$$P = \frac{l}{p_2} \left(\frac{dQ_1}{dt} \right)_{ss} \quad (5)$$

where p_2 is the upstream gas pressure and when the downstream pressure is essentially zero. Since $P = DS$, it is possible to compute all three coefficients from graphs like Fig. 1 using Eqs. 4 and 5.

Since in the above case the membrane is initially “empty,” i.e., $C_0 = 0$, gas must be absorbed by the membrane to reach steady state so Eq. 4 defines what might be called the “absorption time lag,” i.e., θ^a . For the alternate case where $C_0 = C_2$, gas must be desorbed to reach steady state so there is a “desorption time lag” which is given by

$$\theta^d = -l^2/3D \quad (6)$$

Petropoulos and Roussis have defined other time lags and evaluated various relationships among them for a wide variety of complex situations (Petropoulos 1967). Barrie et al. evaluated the time lag for laminated membranes using the Laplace transforms (Barrie et al. 1963). Frisch developed a useful mathematical procedure for constructing asymptotic solutions for permeation problems, hence time lags, for more complex situations where full solutions to Fick’s second law are not feasible (Frisch 1957), e.g., when the diffusion coefficient depends on penetrant composition or position in the membrane or when chemical reactions or adsorption processes occur.

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Tissue Engineering and Regenerative Medicine

► Bioartificial Organs and Tissue

Tissue Engineering, Membrane Operations of

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Synonyms

Biofabrication; Biohybrid membrane systems; Regenerative medicine

The first and the most common definition of tissue engineering states that it is “an interdisciplinary field that applies the principles of engineering and life sciences toward the development of biological substitutes that restore, maintain or improve tissue function or a whole organ” (Langer and Vacanti 1993). In other words, tissue engineering combines the principle of materials and cell transplantation to develop new tissues and/or promote endogenous regeneration. Living and functional cells are implanted or “seeded” into an artificial substrate or *scaffold* able to give them specific cues and to recapitulate the *in vivo* milieu of their own microenvironments, driving and supporting three-dimensional tissue formation. With the purpose of producing functional replacement tissues for clinical use, the principles of

tissue development and growth must be understood and applied. On the other side, the supporting materials, both *ex vivo* as well as *in vivo*, are critical and crucial to engineer living tissues. They allow cell adhesion and migration, exert specific mechanical and biological influences able to modify cell shape and functional behavior, and at the same time enable the delivery and diffusion of biochemical factors, cell nutrients, and products. To achieve these purposes and the goal of tissue reconstruction, scaffolds must meet some specific requirements.

Among artificial scaffolds, polymeric membranes are notably suitable as supporting material in tissue engineering, thanks to their characteristics of stability, biocompatibility, and selective permeability. Polymeric membranes could mimic the extracellular matrix (ECM) with which cells interact, allowing the organization of cells in a three-dimensional architecture. Membranes are able to modulate the adhesion, proliferation, and differentiation of cells and the selective transport of metabolites and nutrients to cells and removal of catabolites and specific products from them (Morelli et al. 2009). Material properties and characteristics as well as surface chemistry and topography strongly impact and affect cell-material interaction and thereby cell response and tissue formation. The cell-material interaction is a complex and dynamic multistep process that mimics natural interactions of cells with their natural ECM. It consists of early events, such as adsorption of proteins from *ex vivo* cell culture media or from *in vivo* biological fluids, followed by cell adhesion, due to the recognition of the EMC components by cell receptors, and cell spreading engendered by cytoskeleton rearrangements. Successively, late events are related to migration, growth, differentiation, and functional activation of cells. Among cellular functional activities, ECM secretion and deposition by the same cells strongly contribute to the tissue growth and maturation.

Thus, the choice of membrane materials and membrane properties is crucial to engineer target tissues. A high *porosity* and an adequate *pore size* are necessary to foster both cell adhesion and

diffusion of nutrients and metabolites. *Surface properties* and *morphology* influence the adsorption of proteins and their conformational changes and therefore cell adhesion. Protein adsorption is favored on rough surfaces rather than the smooth ones. On the other hand, smooth surfaces elicit more organized ECM deposition and more homogeneous distribution of focal adhesion. *Surface physicochemical properties* such as *wettability* and *free-energy parameters* predict membrane cytocompatibility. A proper and suitable cell adhesion takes place on surfaces with a moderate hydrophilicity. Extremely hydrophilic surfaces bind too loosely the proteins that mediate cell adhesion, while otherwise, extremely hydrophobic surfaces strongly absorb proteins perturbing their natural folding with distortion of cell receptor-binding domains. Moreover, roughness, pore size, and porosity, as well as proper pore shape and distribution, influence and enhance a rearrangement of cytoskeleton proteins that trigger the extrusion of pseudopodia from cells. These latter ones work as anchorage points for the formation of focal adhesion complexes and for cell motility, favoring cell-material and cell-cell interactions. *Topographical cues*, including grooves, ridges, steps, pores, wells and nodes, drive the cell orientation and migration and influence the organization of cytoskeleton rearrangements and consequently the cell shape. Micro-topographies could influence cell differentiation and gene expression. In neuronal tissue engineering, patterned membranes promote an oriented peripheral nerve growth (Morelli et al. 2010). A pivotal role in cell response in tissue reconstruction is played furthermore by *mechanical properties* of the supporting materials. During tissue formation, mechanical stresses play in control of cell phenotypes or “fates”, such as growth, differentiation, motility, and apoptosis. Also in tissue repair, the tissue development is actively regulated by the spatial organization and by the mechanical constraints imposed on cells (Petreaca and Martins-Green 2014). In tissue engineering, the mechanical properties of materials strictly depend on the tissue that has to be reconstructed: hard tissues such as the bone

necessitate stiff matrices and soft tissues such as tendons, ligaments, skin, fibrous tissues, muscles, nerves, and blood vessels need more elastic and flexible scaffolds. Cell spreading, proliferation, and migration are enhanced on stiffer substrates than soft ones. Many kinds of cells, like neurons, chondrocytes, fibroblasts, and vascular smooth muscular cells, migrate to stiffer region if cultured on a rigidity gradient. On polymeric membranes, an enhanced tensile modulus and strength and a high porosity are able to promote capillary development by endothelial cells (Salerno et al. 2011).

Since an efficient metabolite and nutrient transport is required for the long-term maintenance of cell viability and functions, an important tissue engineering challenge is to evaluate diffusive and convective contribution to mass transport (Curcio et al. 2005). *Transport properties* and *permeability* of membranes influence tissue reconstruction and regeneration through the diffusion of nutrients and secreted soluble factors. Specie transport through a membrane takes place because of a difference in chemical potential: difference in concentration, temperature, pressure, or combination of these variables. In the absence of solutes, the hydraulic permeance is related to the fluid viscosity and to membrane properties such as thickness, pore size and porosity, pore geometry, and tortuosity. Mass transfer through membranes in a multicomponent system with solutes and solvent occurs as a result of the differences in static and osmotic transmembrane pressures. The transport of nutrients and metabolites with a low MW occurs by diffusion, whereas macromolecular species and proteins follow a convective transport. The driving forces for diffusive and convective transport are transmembrane concentration and pressure gradients, respectively. The transport of solutes through porous membranes depends not only by transmembrane gradients but also by the size and shape of solutes related to membrane pore size and thickness. Specific physicochemical solute-membrane interactions such as electrostatic, hydrophobic, or acid-base interactions can also influence the transport across membranes.

The use of biodegradable polymer for the synthesis of biodegradable membranes represents an additional key for the development of successful implantable bio-artificial constructs. *Biodegradability* is often a requisite factor since scaffolds should be absorbed by the surrounding tissues without their surgical removal. A programmed and predictable biodegradation rate has to be consistent as much as possible with the tissue formation rate: this means that while cells are fabricating their own natural matrix structure around themselves, the scaffold should be able to break down leaving the newly formed tissue.

Cross-References

- [Bioartificial Organs, Membrane Operations of](#)
- [Bioartificial Organs and Tissue](#)
- [Biodegradable Polymer for Membranes](#)
- [Biohybrid Membrane Systems](#)
- [Membrane Artificial Organs](#)

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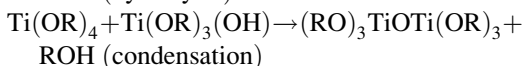
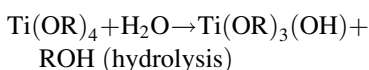
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Titania Membranes

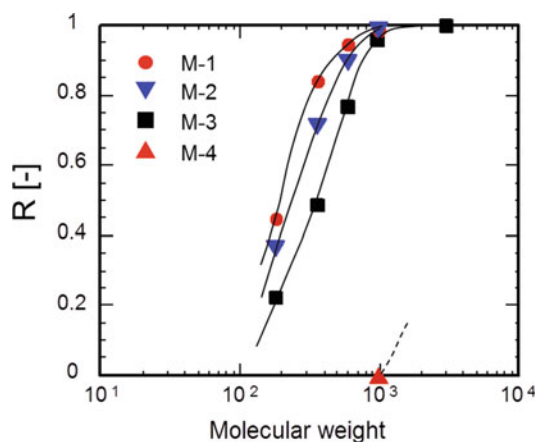
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Titania membranes show excellent chemical resistance and can be used in both acidic and basic pHs, and moreover, they show interesting photocatalytic activity. Titania ultrafiltration membranes have been commercialized by several companies. At present, extensive efforts have focused on the preparation of porous membranes having small pore sizes in the NF range (1–2 nm). Since pore sizes are believed to be controlled by the sizes of the packed particles, controlling the sol size is a crucial process for membrane processing. Anderson et al. [24] prepared nano-sized TiO_2 and ZrO_2 particles (3–5 nm) by carrying out hydrolysis and condensation reactions of metal *tert*-amyloxide with a small amount of water (molar ratio of $\text{H}_2\text{O}/\text{Ti} = 3–5$) in *tert*-amyl alcohol solutions. Hydrolysis and condensation reactions of metal alkoxides are written as follows:



Since both reactions take place by nucleophilic substitution, the electronegativity and the size of alkoxy groups are important. By using a large branched alkoxy group (*tert*-amyl alkoxide), the reaction rate can be reduced, resulting in small-sized sols. An amorphous phase predominated in the xerogel dried at room temperature and fired at 300 °C, and phase transition from amorphous to anatase and from anatase to rutile occurred from 300–400 °C to 400–600 °C, respectively. Therefore, it is important to control firing temperature in order to obtain controlled pore sizes of membranes. Titania membranes which were coated on porous alumina membranes and fired at 200 °C showed approximately a 100 % rejection



Titania Membranes, Fig. 1 Molecular weight cutoff curves for TiO₂ porous membranes (solutes: sugars, 500 ppm) (Wildman et al. 1993)

of polyethylene glycol 200 (PEG200, M. W. 200), depending on operating conditions (Xu et al. 1993). Another strategy for controlling MWCOs is the appropriate choice of sol diameters, which is used at the final coating for the separation of the top layer. (Tsuru et al. 2001) successfully prepared a variety of MWCOs for TiO₂ membranes at the same firing temperature of 450 °C using sol solutions having different sizes of sol diameters, as shown in Fig. 1. M1, M2, and M3 show MWCOs approximately 500, 600, and 800, while M4 shows nearly no rejection for α -dextrin (MW 972).

On the other hand, Société des Céramiques Techniques (SCT) claimed that they had commercialized TiO₂ NF membranes having an MWCO of 1,000 (Sarrade et al. 1996) based on research work by Commissariat à l'Energie Atomique (CEA). Colloidal sols with a diameter of 15 nm, which showed an anatase phase and which were stable up to 600 °C, were coated on porous alumina supports and fired at 500 °C. Voigt et al. (Puhlfürß et al. 2000) prepared polymeric sols from a solution of Ti-isopropoxide in isopropyl alcohol by the addition of a small amount of water. NF membranes, which were prepared by coating the polymeric sols on a TiO₂ intermediate layer (pore size 5 nm, prepared by colloidal TiO₂ sols), followed by firing at 450 °C, had an MWCO of 480 and a pure water flux of 20 l/(m² h bar) and

were applied to the separation of electrolytes. Benfer et al. (2001) also developed TiO₂ NF membranes by the polymeric sol route. Tetraethyl orthotitanate was partially hydrolyzed at conditions where the molar ratio of water over the alkoxide was less than 1, followed by the addition of an acid or organic base to control the viscosity of the polymeric sol solution, i.e., the size of the polymeric network. They also prepared zirconia porous membranes by the same method. Filtration performance of TiO₂ membranes shows comparable water permeabilities to those of polymeric NF membranes.

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Toluene Removal by PV on Polymeric Membranes

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Synonyms

[BTEx removal by PV on polymeric membranes](#)

Toluene is one of the volatile organic compounds (VOCs) that cause serious damage to human and animal due to their toxicity (Satyanarayana et al. 2004). The other chemicals in this category include benzene, xylenes, ethylbenzene, etc. They are collectively called as BTEX, a word composed of their initial letters. Elimination of BTEX from water, therefore, is a mandatory nowadays.

These chemicals can move freely in water and air; their sequestration is relatively difficult. Air stripping and activated carbon adsorption processes are the conventional methods for removal of BTEX from water. In recent years, a new focus for separation of BTEX from wastewaters is pervaporation. Pervaporation is a membrane process that performs molecular-scale liquid/liquid separation. It is carried out by maintaining the downstream pressure lower than the saturation pressure of the liquid at that temperature. A vacuum or gas flow is used at the permeate side to achieve the lower pressure. With the dense structure of the membrane, the interaction between membrane material and penetrant is critical to the separation efficiency. The mechanism for penetrant transport through the membrane is the solution–diffusion model, which assumes instant desorption at the permeate side of the membrane. In many researches for separating benzene, toluene, ethylbenzene, and xylenes (BTEX), toluene is used as a representative chemical (Satyanarayana et al. 2004). This approach using single chemical may give a more clear insight into the mechanism of pervaporation. The concentration of VOCs in wastewater is low. Therefore, hydrophobic membranes preferentially removing organics are much more cost-effective than hydrophilic ones. Polydimethylsiloxane (PDMS), ethylene–propylene diene monomer (EPDM), and polyether block amide (PEBA) are typical hydrophobic polymers (Blume et al. 1990; Sampranpiboon et al. 2000b; Viswanathan et al. 1995). High permselectivity of these materials is attributed to its stronger affinity for BTEX than for water. Their polymer chains are dominated by nonpolar functional groups, thus moving freely and providing high free volumes in the membrane. That is the

reason for high diffusion of organics across the membrane. To improve membrane hydrophobicity, the methyl groups are replaced by long alkyl groups in the side chains (Sampranpiboon et al. 2000a). Poly(1-(trimethylsilyl)-1-propyne) (PTMSP) is found to be much more organophilic; however, both the flux and the selectivity decreased as operation proceeds (Fadeev et al. 2000). Inorganic materials have already shown good performance in alcohol recovery, but not many reports are regarding their application in BTEX removal. The reason might be that the high production cost and the reward from wastewater treatment are skewed. In order to get materials having better performance, therefore, mixed matrix materials with inorganic particle-filled hydrophobic materials are designed (Boom et al. 1998; Panek and Konieczny 2009).

Due to their poor performance in mechanical property, hydrophobic polymer-based materials are generally made into composite membranes with a porous sublayer supporting their ultrathin dense layer. The support layers for removal of toluene from water are mainly fabricated from polysulfones, polyetherimides, polyimides, polyacrylonitriles, and polyesters that have good mechanical strength and high resistance toward the swelling of organics (Peng et al. 2003).

As mentioned above, activated carbon adsorption is a more widely used technology. But it has disadvantages such as requirement to alternating recovery steps. Also, the operational costs in air stripping are high due to the necessity to posttreatment stages for preventing water pollution into the air pollution. Likewise, pervaporation has its drawbacks. It is practical for pervaporation to recover highly dilute organic compounds in water (i.e., <10 ppm), as a result of the exponential increase of membrane area needed to yield economical productivity. Nevertheless, adsorption and air stripping are well suited to even lower concentrations. Therefore, any process design should attempt to consolidate the advantages of each technology while overcoming their individual limitations, so that separation targets otherwise unrealistic can be achieved.

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- (Kocherginsky et al. 2007). At the feed-membrane surface, the component having physical or chemical affinity with the liquid or the chemicals inside the liquid (e.g., carrier) will be selectively sorbed and diffuse across the membrane. At the other surface of the membrane, the component is released from the liquid as a result stripping by the permeate fluid. Liquid membranes (LM) are broadly classified into three types: bulk, emulsion, and supported liquid membranes (SLM). In SLM, liquid for selective transport is imbedded inside the porous part of a solid (e.g., polymer) support and is kept there by capillary forces. Pervaporation (PV) through SLM applies vacuum or gas flush at the permeate side of a SLM to facilitate desorption of the organics from LM.

A new type of a hollow fiber contained liquid membrane (HFCLM) PV system was employed to separate some toxic VOCs such as trichloroethylene and toluene from water (Yang et al. 1995). In this design the highly selective organic LM is contained in the shell side between two sets of hollow fibers packed in a shell-and-tube heat exchanger arrangement. Wastewater is fed into one set of hollow fibers and vacuum is applied in the other set of hollow fibers. The separation factors and solute recoveries for the HFCLM system were higher and water fluxes lower than in a conventional pervaporation system based on silicone rubber with vacuum applied outside the silicone rubber hollow fibers. The effluent concentration data for the HFCLM were satisfactorily correlated with a material balance where the mass flux was expressed in terms of an overall mass transfer coefficient based on resistances-in-series model.

PV through SLM is a unit process involving extraction and stripping steps simultaneously. The benefits of using an LM in pervaporation are the high selectivity and specific molecular recognition achieved with the liquid and carriers possibly contained, which will reduce the energy required for the BTEX recovery. However, there are very few investigations on PV using SLM (Qin et al. 2002). The reasons can be attributed to the

Toluene Removal by PV Supported Liquid Membranes

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Liquid membrane (LM) uses a thin layer of liquid as the media to preferentially transport specific component from one side to the other

well-known problem of instability of SLMs in applications. The SLM might not provide a stable organic flux, arising from the possible dissolution of LM into water phase. Further, the solid support is significantly swollen by the liquid it contains inside to such a degree that the mass transfer through it is not negligible. Consequently, the support will also influence the selectivity of the SLM.

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Tomographic Microscopy Methods

► 3D-Imaging Methods for Membranes

Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices

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Synonyms

[Electrochemical deposition](#); [Galvanic replication](#);
[Nuclear track filters](#)

Introduction

In the fast developing technologies era, nanotechnology is the one significant technology that has already taken a big leap. It appears to be all set for bringing in revolution in the development and advancement of techniques involved in the synthesis and fabrication of sensors and devices with great potential. The conventional microelectronics fabrication techniques are facing very harsh competitions from low dimensional strategies helping “Moore’s Law” survive and bringing down the high costs. The conventional techniques for fabrication of very low dimensional wires – say quantum wires – include wet chemistry, electron beam lithography, focused ion beam techniques, and atomic-beam lithography (Huixin). That has shown the ways for adopting newer alternative approaches which are relatively inexpensive, easier to handle, and synergistically adorned with high efficacy. Nanotechnology is one of the fastest growing new areas in science and engineering and deals with science and technology associated with dimensions in the range of 0.1–100 nm. The subject arises from the convergence of electronics, physics, chemistry, biology, and materials science to create new functional systems of nanoscale dimensions. The ability to fabricate structures with nanometric precision is of fundamental importance to any exploitation of nanotechnology. Nanotechnology is predicted to have a major impact on the manufacturing technology in the next few decades from now.

It is now well known that size of the devices and components dictate many unusual traits and characteristics where quantum effects become more predominant. In the recent years, there has been a tremendous spurt in the potential applications of metallic as well as nonmetallic nano-/microstructures and materials. Quasi-one-dimensional nanostructures and materials like nanowires, fibers, tubules, etc., having high aspect ratio, would provide unusual and uncommon properties like strength and hardness enhancement, dramatic changes in electrical conduction, field-ion-emission through tunneling phenomenon, optical, magnetic, and chemical, and other important functional attributes which are found to

be enhanced when the size reduction comes into play. Materials with nanoscopic dimensions may exhibit quantized conductance (Landauer 1989) which not only has potential technological applications in various areas but also is of fundamental interest.

It has been approximately five decades since researchers first began exposing materials like polymers to ionizing radiation and reporting the occurrence of cross-linking and other useful effects. Today, a substantial commercial industry is in place based on processing of polymers with radiation. Innovation in this field has by no means ended; important new products made possible through radiation technology continue to enter the marketplace, and exciting new innovations in the application of radiation to macromolecular materials are under exploration at research institutions around the world.

This entry reviews the technique – the “template synthesis” (TS) – involving the porous membranes (specific reference is made to track-etch membranes) which are spin-off from the radiation-matter interaction and are used as tools in the development of nano/micromaterials, structures, and devices. The recent past has witnessed the keen interest being generated on the use of innovative technologies like TS in the production of nanomaterials’ fabrication involving materials like metals, nonmetals like semiconductors, magnetic multilayered nanowires, conducting polymers, glasses, nanotubules, wires, whiskers, etc., reported from various authors and from our lab (See refs in (Chakarvarti and Vetter 1998; Martin 1996; Brumlik et al. 1994; Chakarvarti and Vetter 1993; Kumar et al. 2004a, b, c, d, e, f; Sekhon et al. 2004; Kumar et al. 2005; Chakarvarti et al. 2005a; Kumar and Chakarvarti 2005; Chaudhri et al. 2006a; Singh and Chakarvarti 2008a; Chakarvarti 2007a; Kumar and Chakarvarti 2007a; Chakarvarti 2007b; Kumar et al. 2007a, b; Chaudhri and Chakarvarti 2008a; Kumar et al. 2008a)).

Nano Synthesis Approaches

All the conventional and available nanosynthesis techniques can be categorized into two complementary approaches:

- The top-down approach – starting with the bulk material and carving the way down to the nanoscale, and
- The bottom-up approach – starting at the molecular level and fabricating up the material through the small cluster level to the nanoparticle and the assembly of nanoparticles.

Nanotechnology provides the ability to fabricate structures with nanometric precision that is of fundamental importance. The potential of combining radiation effects with nanomaterials has been recognized from the very early stages of nanoscience research. In the many uses of nanostructures, and nanoparticles in particular, from catalysis, bio-sensing, nano-electronics, magnetic applications including separations, mechano-chemical conversion, and to molecular computing radiation can play a significant role.

Many nanostructured systems, like metal sulfide semiconductors of nanometric matrices, PC-controlled biochips for programmed release systems, nano-ordered hydrogels based on natural polymers, development of polysaccharides, emerge out from the use of radiation (UV beam, electron beam, or focused ion beam) techniques which offer unmatched reproducibility and very narrow size distribution. The relative advantages and deficiencies of each of them are still to be clarified as the technology advances. However, whether UV or electron beam will lead to the highest resolution is still debated.

The studies on natural rubber-clay composites and thermoplastic natural rubber-clay composites have given interesting results. Nanomaterials with high abrasion and high scratch resistance will find industrial application.

The formation of microporous and nanoporous membranes having highly uniform geometry and precisely determined structures is an exciting example of industrial application of ionizing radiation. These materials, called track-etch membranes (TEMs) were first made by irradiation of polymeric sheets, micas, and glasses with fragments from the fission of heavy nuclei such as californium or uranium (nuclear track-etch method). This technique presents a great limitation due to contamination of the foil with

radioactive products so that “cooling” of the irradiated material, before using, is needed; this usually takes a few months. The second method makes use of heavy ion beams, usually of energy on the order of several MeV, from accelerators and presents quite a few advantages over the former one which are: (a) no induced radioactivity in the irradiated material when ion energy is below the Coulomb barrier; (b) all tracks show the same etching properties; (c) deeper penetration in the material owing to higher energy of particles; (d) higher density (even $>10^9 \text{ cm}^{-2}$ for smaller pores) track arrays; and (e) easier control of the impact angle and production of arrays of parallel tracks. A heavy ion beam with acceleration energy of more than 1 MeV/n deposits its energy to a substrate in a region $<10 \text{ nm}$ in diameter (an ion track); the depth of the affected region can be regulated by changing the energy or replacing species of ion particles. Widely used polymers for ion track membranes are polyethylene terephthalate (PET) and polycarbonate (PC). By bombarding PET or PC films with swift heavy ions (e.g., Ar^+ , N^+ , or Xe^+) latent radiation damage linear tracks are created through the samples.

According to the following sensitization and etching with an alkali solution (NaOH for instance), uniform cylindrical, conical, tunnel-like, or cigar-like pores have been obtained. Pore sizes or dimensions depend upon various factors, viz., the nature and energy of incident particles, the target material, etch conditions, e.g., temperature, nature of etchant, pre-etch storage conditions, etc., and are controllable.

Cylindrical channel 0.02–5.0 μm in diameter with lengths of 10–50 μm , membranes containing anywhere from a single pore up to $10^9 \text{ pores/cm}^{-2}$ have been produced, and thin film polymer membranes having highly uniform pore size and a wide variety of porosities in well-distributed areas of the template (patterning) are already commercially available. A number of modification methods have been devised for creating TEMs with special properties and functions.

These isoporous membranes are used as template materials for the synthesis of micro- and nanostructures. The template-base method consists of filling a host porous medium with one or

more desired materials. Three main processes are used for the synthesis of various combinations of polymers and/or metals:

- (a) electrodeposition, where one side of the template coated with a metallic layer, or the template support itself, is used as a cathode for electroplating; (b) chemical polymerization where a solution of the desired monomer and initiator, in which the template membrane is dipped, is left to diffuse through the pores of the templates leading to a polymerization reaction in these pores; (c) electroless plating where a catalyst to the pore walls is applied which facilitates the deposition of metal on the activated pores of the template. The micro- or nanomaterials, which are produced in this way, take the form of wires or tubules. Magnetic, conducting, and superconducting nanowires and nanotubules in array or isolated mode possessing special properties have been manufactured in this way.

There are two distinct nano-fabrication processes using heavy ion beams; one is nano-hole formation due to the damage of ion beam path, and the other is nanowire formation due to cross-linking of polysilane, which is also caused by heavy ion beams. Potential applications in devices such as microwave filters for shielding microwave ovens and mobile phones, or in chemical detectors and biosensors with conductive polymer nanotubules are also being seriously considered.

The fabrication of ion track membranes made of PET has been reported to develop selective membranes for the separation of toxic metal ions, biomolecules, and biological cells because of the advantages to control the pore size and the properties of the internal surfaces of the pores.

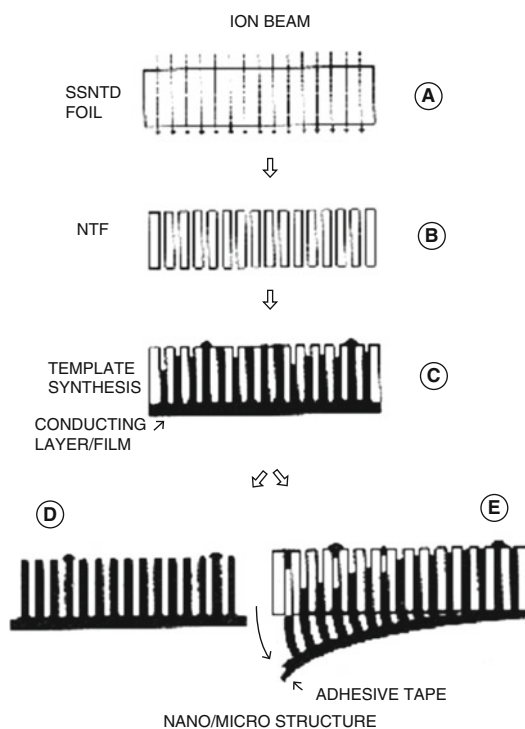
Methodology

Track-Etch Membranes (TEMs)

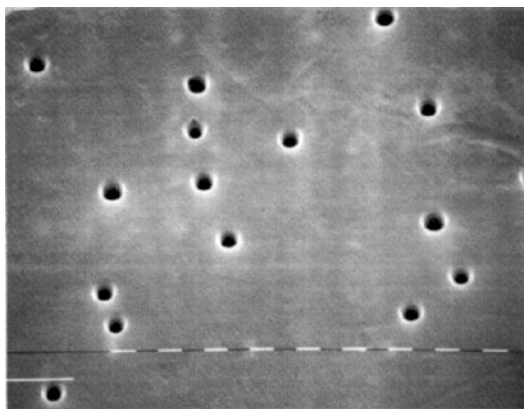
The most widely used materials in manufacturing TEMs are polymers, micas, and rarely this glass sheets. TEMs, also known as nuclear track filters (NTFs), have emerged as spin-off from solid state

nuclear track detectors (SSNTDs) – solid dielectric materials capable of storing damage trails of energetic heavily ionizing ions which can subsequently be chemically amplified for observation as pores either through, say SEM or optical microscope. The art and science used in crafting of TEMs as templates involves two steps – irradiation of an SSNTD foil or a film by heavy energetic ion beam creating damage trails, also called as latent tracks and, followed by a controlled chemical etching of these latent tracks so as to produce see-through pores in the host material. The size and dimensions of the etched pores can be controlled conveniently through parametric control over the nature and energy of the intruding ions, the host material as target to be developed as template, chemical etch conditions, viz., nature, concentration, temperature, agitation, etc., besides preirradiation and postirradiation storage conditions of the target material. The etched pores can have diameter ranging from few nm to mm. NTFs have been put to numerous other applications besides their use as templates. There exists a wealth of literature on SSNTDs and related topics. As discussed already, a large number of materials are used in manufacturing of NTFs which include mainly polymeric sheets, micas, glasses, etc. The particle track-etch technique, therefore, enables the generation of definite shaped pores which can either be used individually in the form of single particle track or collectively in the form of pore arrays constituting many pores – distributed either stochastically (pore density as high as $10^{10}/\text{cm}^2$), or in a well-defined spatial geometry through the control of the drilling particle beam used in “write mode.” Areal dispersion usually lies between 2 % and 20 % and a 10 MeV/nucleon heavy ion (say, for example, various projectiles used are collimated beam of fission fragments, heavy energetic ions like U, Pb, Ag, Si, Bi, etc., whose range in the target material is far greater than the thickness of the target) has a range of the order of 10 μm in many polymers (Williams and Giordano 1984). The custom made NTFs are available in a wide variety of pore size and porosities. The crafting of TEM templates through ions has been discussed in details (see for example, (Possin 1970; Williams and

Giordano 1984; Klien et al. 1993); etc.). Handled adequately and properly, these TEMs can enable wires, tubules, solid cylinders, conical or tapered needles, etc., with a well-controlled dimension and shape besides a large aspect ratio. The dimensional parameters can vary from 10 nm to several micrometers with aspect ratio as high as 10–1000. The pores can be “drilled” with alignment in any direction depending upon the angle of incidence of the beam with the target. The synthesized members may either be left within the pores as embedded or can be removed either by dissolving or removing the host or pulling out mechanically but carefully of the host matrix. Figure 1 shows



Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 1 Schematic diagram showing production of a TEM as a template for synthesis of low dimensional template with monodispersed pores of dia structures. (a). Polymeric foil being irradiated with heavy and energetic ion beam, (b) chemically etched foil as template or an NTF (c), deposited metal ions into the pores, producing filled pores, (d) free-standing structures after removal of host template, and (e) mechanical peeling, an alternative to dissolution or removal of the host for retrieval of synthesized structures



Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 2 A processed TEM with pore dia ca. 1 nm

schematically the process of producing TEM and its use as template, and Fig. 2 shows SEM photograph of a processed polycarbonate (Makrofol) NTF with monodisperse pores.

Template Synthesis: A Technique

The template approach has been extensively investigated in the synthesis of various nanostructures. For example, mesoporous oxides with well defined and ordered porous structure can be readily synthesized using surfactant or copolymer micelles as templates through sol-gel processing. However, template-based synthesis is most commonly and widely used to prepare free standing, nonoriented and oriented nanowires, or nanorods or nanotubes; the latter is also referred to as nanorod or nanowire or nanotube arrays. The most commonly used and commercially available templates are anodized alumina membrane (AAM) and radiation track-etched polycarbonate (PC) membranes. Other membranes have also been used, such as nanochannel array on glass, radiation track-etched mica, mesoporous materials, porous silicon by electrochemical etching of silicon wafer, zeolites (Ozin 1992), and carbon nanotubes. Bio-templates are also explored for the growth of nanowires and nanotubes such as Cu, Ni, Co, and Au nanowires. The commonly used alumina membranes with uniform and parallel pores are made by anodic oxidation of aluminum sheet in solutions of sulfuric, oxalic, or

phosphoric acids. The pores can be arranged in a regular hexagonal array, and densities as high as 10^{11} pores/cm² can be achieved. Pore size ranging from 10 nm to 100 μ m can be made. PC membranes are made by bombarding a nonporous polycarbonate sheet, typically 6–20 μ m in thickness, with nuclear fission fragments to create damage tracks and then chemically etching these tracks into pores. In these radiation track-etched membranes, pores have a uniform size as small as 10 nm, but they are randomly distributed. Pore densities can be as high as 10^9 pores/cm². In addition to the desired pore or channel size, morphology, size distribution and density of pores, and template materials must meet certain requirements. First, the template materials must be compatible with the processing conditions. For example, an electrical insulator is required for a template to be used in electrochemical deposition. Except for the template-directed synthesis, template materials should be chemically and thermally inert during the synthesis and following processing steps. Secondly, depositing materials or solution must wet the internal pore walls. Thirdly, for the synthesis of nanorods or nanowires, the deposition should start from the bottom or one end of the template channels and proceed from one side to another. However, for the growth of nanotubules, the deposition should start from the pore wall and proceed inwardly. Inward growth may result in the pore blockage, so that should be avoided in the growth of “solid” nanorods or nanowires. Kinetically, enough surface relaxation permits maximal packing density, so a diffusion-limited process is preferred. Other considerations include the easiness of release of nanowires or nanorods from the templates and of handling during the experiments. AAM and PC membranes are most commonly used for the synthesis of nanorod or nanowire arrays. Both the templates are very convenient to use during the growth of nanorods by various growth mechanisms, but each type of template also offers a few disadvantages. The advantage of using PC as the template is its easy handling and easy removal by means of pyrolysis at elevated temperatures, but the flexibility of PC is more prone to distortion during the heating process, and the

removal of the template would occur before complete densification of the nanorods. These factors would result in broken and deformed nanorods. The advantage of using AAM as the template is its rigidity and resistance to high temperatures, allowing for the nanorods to densify completely before removal. This would result in a larger surface area of fairly free-standing and unidirectionally aligned nanorod arrays. The problem with AAM is the complete removal of the template after nanorod growth, which has so far been unsuccessful using wet-chemical etching.

The technique of TS (Ozin 1992) may be classified into three categories depending upon the mode of use of templates (Huixin): the negative template method, positive template method, and surface step-edge template method. The negative template method which is the most popular and widely used techniques of TS allows the use of prefabricated nanopores in solid templates, and the material is deposited into these pores normally using electrochemical techniques. After removing (say by way of dissolving) the host template, free-standing elements as wires, cylinders, or conical structures can be obtained. The method has been regarded as “brute-force” method as the synthesized ensemble structure depicts the true replication of the morphology of the pores (Foss 2002). The fabrication of such templates involves many techniques including heavy ion irradiation of solid insulating materials like polymeric foils, micas, glasses, etc., producing so-called TEMs. More details would follow later. The positive template methods use wire-like substrates like DNA (size ca. 2 nm) (Braun et al. 1998), carbon nanotubes (Fullam et al. 2000), etc., on the outer surface of which the material is deposited to the desired dimensions. The removal of templates can produce wire-like or tube-like structures. Other positive templates have been discussed by Huixin He and Nongjian J. Tao (Huixin). The surface step-edge templates, also known as “step-edges decoration,” use the fact that there is preferential or selective deposition of many materials initiating on the defect sites. Zach et al. (Zach et al. 2000) and Bera et al. (Bera et al. 2004) used this technique for generating conductive metal oxide (MoO_x) at the step-edges of HOPG, which after reduction in

appropriate environment could yield metallic Mo nanowires.

When electrodeposition is carried out, the nucleation of nanostructures on the electrode substrate via template pores during electrodeposition is influenced by the crystal structure of the substrate, specific free energy, and other factors like adhesion energy; orientation of the lattice of the substrate; etc., and the final size distribution of electrodeposits is strongly dependent upon the growth and nucleation kinetics (Bera et al. 2004). Template-assisted electrodeposition process can be divided into two categories: active template-assisted process which results from growth of nuclei that essentially nucleate at the pores and defects of the substrate, while the other is known as restrictive template-based electrodeposition used mostly in the synthesis of metallic nanowires, involves deposition of metal into the prefabricated and designed pores within an inert, insulator membrane or template. PTM, porous alumina, conductive polymers, carbon, etc., have been used as templates which fall under this category (Bera et al. 2004).

Negative Template Synthesis

The basic and underlying principle of negative TS is similar to that of producing materials through the use of replication, e.g., die-casting or molding like making ice candies. There are many methods used in practice for preparing nanomaterials right from milling to lithographic techniques (Hhadjipanayis and Siegle 1994). These techniques suffer from the problems like little control over the final morphology of the resulting nanoproductions, ensembles, and materials. The TS has in turn edge in this regard. It enables the synthesis of a variety of materials ranging from micro- to nanodimensions, high aspect ratio, and of desired morphology and geometry – the single unique attribute which makes this route as most acceptable and economical too. A template, in a general sense, may be defined as a predesigned structure within which a network exists, which can be utilized for further use. Thus, for example, a membrane with prefabricated cavities or pores of known morphology, number, distribution, and configuration may also act as a template; the pores

of which can facilitate replication by any suitable means. Removal of the host template would lead to the presentation of ensembles whose morphological and stereo-chemical features and traits might replicate the original cavities or pores in the template. Here in this technique, materials can be deposited within the cavities or pores or any other dimensional structures, by various methods like electrochemical or chemical reduction (electroless) of the appropriate ion. Depending upon the template geometries and the controlling factors, functional procedure, and related parameters, the generated structures can be monodisperse homogeneous or heterogeneous, multilayered, short, squat fibrils, long needles, hollow tubules, tapered conical (single or double cones) elements, etc., depending upon the template factors stated above. The interesting aspect is that one can have complete control over the aspect ratio (length and diameter ratio). Metallic as well as nonmetallic tubules can be obtained by chemically derivating the pore/cavity walls by providing molecular anchors so that the electrodeposited metal deposits preferentially on the walls layer by layer, leading to hollow tubules when the process is terminated at a preestimated time interval (Martin et al. 1990). The synthesized structures can remain either inside the host structures in the templates or they can be rendered free, and collected as ensemble. Alternatively, an ensemble of nano-/microstructures that protrude from a surface like the bristles of a brush can be produced. The technique is blessed with simplicity and nano-/microstructures with extraordinary low dimensions have been reported to be produced (see refs in Parthasarthy et al. 1995; Schonenberger et al. 1997; Sima et al. 2004) which are otherwise difficult to manufacture using lithographic methods.

History and Development of Negative Template Synthesis

Bean (Bean 1969) first demonstrated the art of filling the pores of a membrane with silver followed by Possin (Possin 1970) who utilized electrodeposition technique in the fabrication of thin wires as small as 400 Å using mica with etched pores as templates for synthesis of such

elements of the nanostructures. Williams and Giordano (Williams and Giordano 1984) claimed to have reduced the size down to 80 Å after effecting some refinements to the technique. Penner and Martin (Penner and Martin 1987) reported on the generation and characterization of ultra-microelectrodes with radii as small as 1000 Å. Klien et al. (Klien et al. 1993) reported on the fabrication of graded CdSe/CdTe heterostructures and development of chemistry for fabricating II-VI chalcogenide semiconductors CdSe and CdTe within the template membranes producing micro-diode arrays consisting of micro-cylinders retinal rod cells – the photoreceptors in the human eye – and having ca. five times smaller diameter than that of photoreceptors. Team led by Prof. Charles Martin at Colorado State University, USA, has been actively engaged in exploring and exploiting the TS for its full potential and a large number of reports are available (see refs in (Huczko 2000)). Researchers at GSI at Darmstadt, Germany (where this author has had also his first hands-on experience with the technique of TS for a short duration during early 1990s), have also many reports to their credit for developing the technique further and generating nano-/microstructures (see, for example, ref. (Spohr 1990)). A large bulk of literature since then has been published on the negative TS and its applications (see refs in (Chakarvarti and Vetter 1998; Huczko 2000; Martin 1994)). This lab has also been reporting from time to time on the synthesis of nano-/microstructures, devices, and tubules using TEMs as templates (see refs. (Chakarvarti and Vetter 1998; Martin 1996; Brumlik et al. 1994; Chakarvarti and Vetter 1993; Kumar et al. 2004a, b, c, d, e, f; Sekhon et al. 2004; Kumar et al. 2005; Chakarvarti et al. 2005a; Kumar and Chakarvarti 2005; Chaudhri et al. 2006a)). Almost simultaneously, the TS also included porous alumina (Al_2O_3) membranes, which are prepared electrochemically from aluminum (the fabrication method of anodic porous alumina started as early as 1950s), and have usually high pore density (as high as $10^{11}/\text{cm}^2$) with pores as small as ca. 5 nm, arranged in hexagonal arrays (Despic and Parkhutik 1989).

Here in the present review, detailed discussion has further been carried only on negative template synthesis using TEMs as templates for synthesis of nano-/micromaterials.

Materials

While sieving properties of porous membranes have been used from as early as some thousands of years, but it is relatively only recently that a technological application like TS of nano-/microstructures has been brought to this process – almost a by-product having no relation with sieving properties. Until recently where the use of positive template synthesis has started, most of the work had been carried out using negative template synthesis involving mainly two types of membranes: TEMs and porous alumina (Al_2O_3). Others include nanochannel array glasses, zeolites, proteins, etc. A wide variety of other nanoporous solids that can be used as templates are cited elsewhere (see, for example, ref. Martin 1994).

Template Synthesis of Low Dimensional Structures and Devices

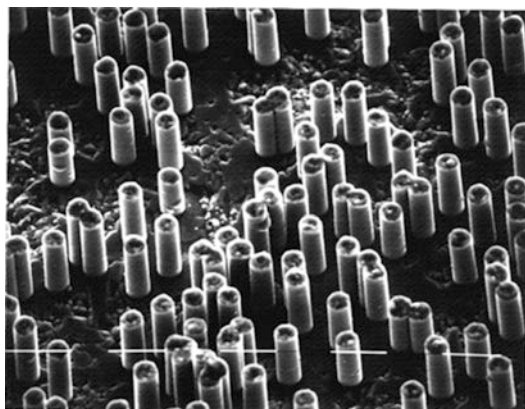
The strategy for embedding matter of interest within the etched pores or channels in the template is the material's placement through some suitable mechanism at the desired places, viz., pores. This can be accomplished in four ways. (Huixin) Using the capillary action of the pores/channels and enabling the solution of the dissolved material entering into the pores, followed by slow evaporation of the solvent. This will lead to growth of supersaturated structural elements (Landauer 1989) using electrochemical (galvanic) technique which is widely practiced. Here, electrodeposition of the desired metal ions is carried out either using two-electrode or three-electrodes electroplating cell (Bera et al. 2004; Chakarvarti and Vetter 1998) using electroless (nongalvanic) deposition technique (Linkot et al. 1999) and references therein (Bercu et al. 2004). The underlying principle is to create nucleation centers on the pore walls and then precipitate the desired material on these nucleation centers. Through controlled

manipulations, one can synthesize hollow as well as solid tubules. Metals like Cu, Ni, Au, etc. or chalcogenides are dissolved in suitable solvents and precipitation can be facilitated on the pore walls. Martin (1996) using chemical reactions, say, by permitting two reagents meet within the pores and react, produced precipitates, followed by drying process and their retrieval (Kumar et al. 2004d). The necessary prerequisite is that the penetrants acting as reactants must be hydrophilic otherwise one would require to apply hydrostatic pressure to forcibly inject them into the pores. In case of two gases (or one as gas and other participant as liquid) as reactants entering from both the faces of the template, the reaction can be accomplished within the pores. For more details, see references in Ferain and Legras (2003).

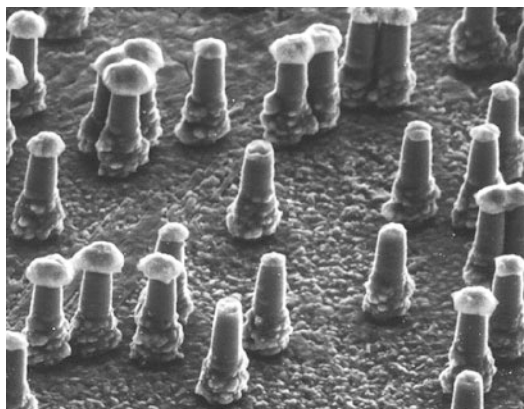
In the proceeding paragraphs, more details of galvanic synthesis only are being provided. As mentioned, the technique is based upon the earlier work of Bean (Bean 1969), Possin (Possin 1970), Spohr (1982), Williams and Giordano (Williams and Giordano 1984) and, Penner and Martin (1987). The simple underlying concept of electro-deposition of metals through electroplating is described as an electrochemical process in which metallic ions in supporting solution are reduced to the metallic state at the cathode, which, if closely covered by an NTF as a template and as an overlay, would lead to the formation of growth of plated film as the embodiment of micro- or nano-structure. The pores of the NTF used would act as template (see Fig. 1).

Electrochemical Cells and Electrodeposition

A scientific treatment of galvanic process is in fact complicated, and development of optimum plating conditions may be obtained through one's personal experience obtained through repeated trials under the given inputs. The age and condition of electrolyte, viz., temperature, pH, concentration, agitation rate, purity of solvent as well as electrolyte solute, additives and their amount, uneven current distribution, increase of specific resistivity of electrolyte, formation of gas bubbles and gas blankets at electrodes excessive inter electrode distance, etc. affect the quality of

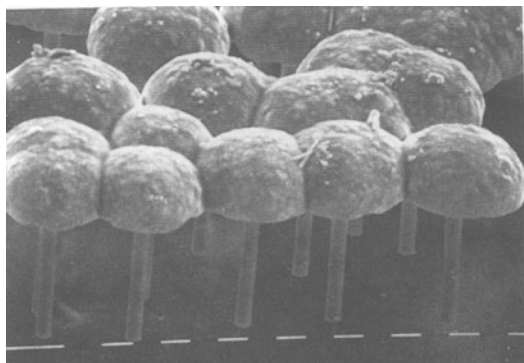


Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 3 Copper microstructures (Chakarvarti and Vetter 1998)



Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 4 Silver conical microstructures (Kumar and Chakarvarti 2005)

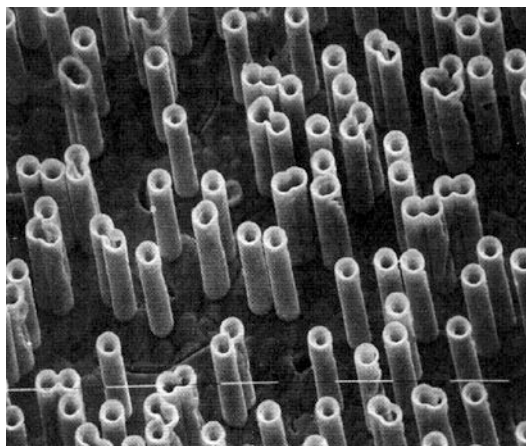
deposition. Plating in small crevices or pores is very difficult. The solutions should have good micro-throwing powers – the ability of a solution to plate into fine cavities or defects on the surface such as pores, pits, polishing lines, and scratches – besides the good covering power, the ability of an electrolyte to deposit metals into pores where current density is low. Copper, for example, has poor macro-throwing power but can possess excellent micro-throwing power. Electrodeposition of metals such as those which are more electronegative (e.g., aluminum, molybdenum, tungsten, titanium, tantalum, zirconium, niobium, etc.) is not always possible from aqueous solutions. Electrodeposition on metals in corrosive electrolytes or galvanic deposition of noble metals such as gold and silver on base metals like copper needs much care as the adhesion of the plated mass is found to be poor. With microporous membranes, rinsing off the membranes with 3 % H_2SO_4 followed by distilled water and absolute ethyl alcohol would facilitate the galvanic process in the case of metals like zinc, indium, etc. (Possin 1970). Presoaking of the cleaned and washed template with the given electrolyte is also helpful (Chakarvarti and Vetter 1991). Many detailed studies of the electrochemical fabrication process for nanostructures have been reported by many workers (Schonenberger et al. 1997; Whitney et al. 1993).



Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 5 Buds and caps as over-deposition

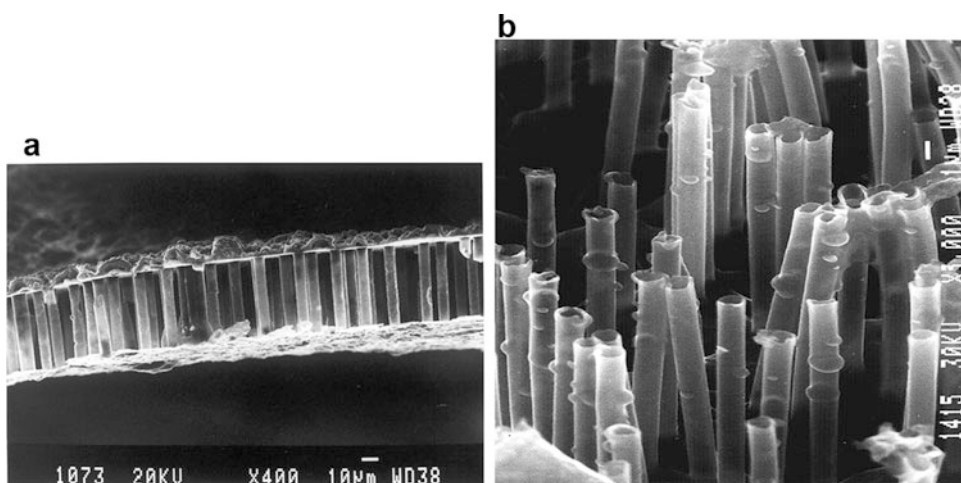
For electrodeposition of metals, some special types of electroplating cells are used (Penner and Martin 1987; Chakarvarti and Vetter 1991; Dobrev et al. 1994) which offer a low ohmic voltage drop across the electrodes even when the cell is filled with a poorly conducting electrolyte. There are various cell designs available: two electrodes and three electrode cells. The cell designed by Dobrev et al. (1994) has the provision for mechanical stirring besides a thermostat for maintaining the desired temperature of the water contained in a jacket surrounding the cell as constant.

Electrodeposition is accomplished by simply coating one face of the overlaid template with a metal film (preferably gold) to serve as a working electrode on which electrodeposition takes place. The thickness of the film is appreciably large if the pores in the templates have also larger size. Alternatively, a metallic tape with conducting adhesive on the surface may also be used for fixing up the template membrane while the pores on the other face act as channel templates with one end sealed (Chakarvarti and Vetter 1991). In order to make

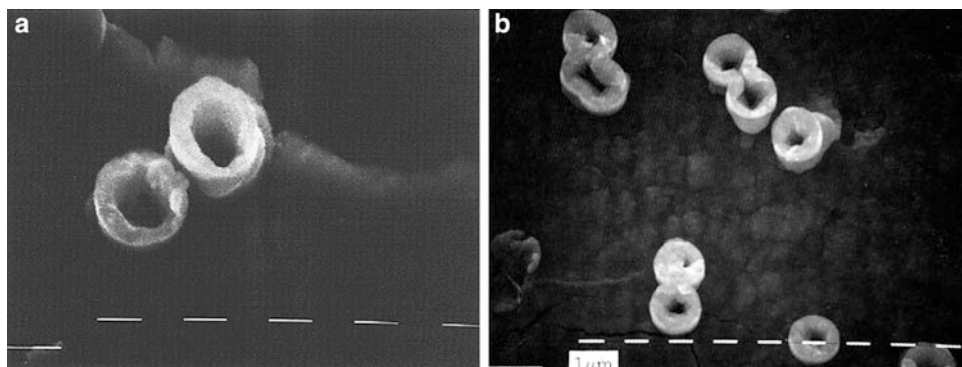


Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 6 Copper hollow tubules

the pore walls conducting so as to be conducive in convenient electrodeposition by way of providing molecular anchors, the template may be moistened with solution like chloroplatinic acid (Penner and Martin 1987) before electrodeposition is carried out. The use of electroless plating on the pore walls of polymeric templates might also be useful before galvanic process is started. This needs etching of polymer surfaces with chromic-sulfuric acid solutions followed by activation by immersion in tin and palladium solutions, or a colloidal solution containing these ions. This process is called “conditioning” which is required to improve the wettability of the polymer surface, which further facilitates adhesion of the plated metal. During electrodeposition of the metal at the cathode, the depletion of the metal ions increases the absolute value of the deposition potential and if this exceeds the hydrogen overvoltage for the given process, hydrogen also deposits resulting into a loss of plating efficiency and increase in pH of the electrodeposited metal, ultimately causing “burning” of the thin deposition. In order to avoid the development of overpotential, factors like increase in bath temperature and the agitation or the electrolyte are helpful. For applying deposition potential and monitoring the current and potential drop across the cell, a good constant voltage (potentiostat) power supply is

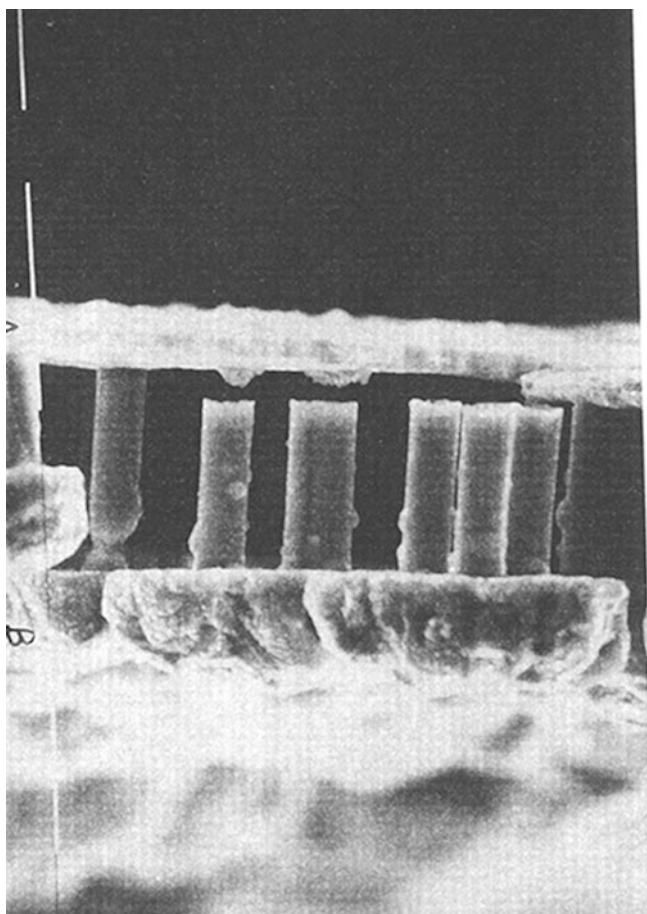


Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 7 (a) Polypyrrole microtubules (Kumar et al. 2004e). (b) Thin walled polypyrrole tubules (Kumar et al. 2004e)



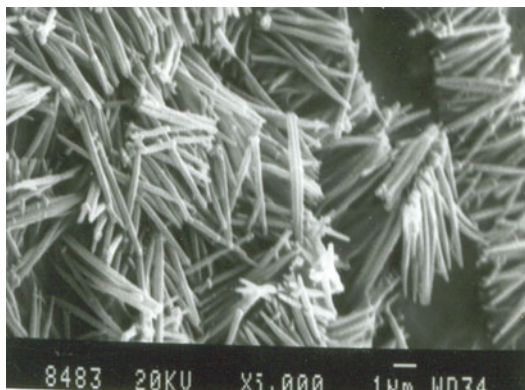
Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 8
 (a) Se microtubules (Chakarvarti and Vetter 1993) (b) Se microtubules (Chakarvarti and Vetter 1993)

**Track-Etch Membranes
 as Tools for Template
 Synthesis of Nano-/
 Microstructures
 and Devices, Fig. 9** Cu-Se
 junctions (Chakarvarti and
 Vetter 1993)

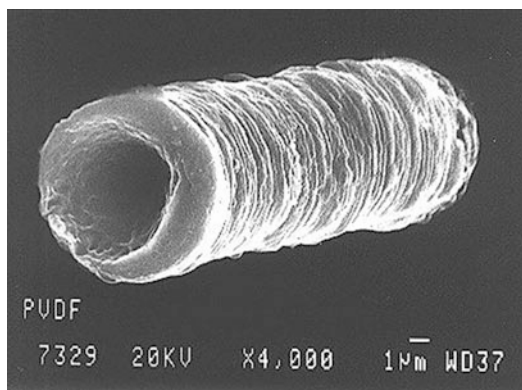


needed. It is found that while DC electrodeposition can produce good quality nanowires, the filling of the pores is partial ca. 10–20 % (Chakarvarti and Vetter 1991). A high filling

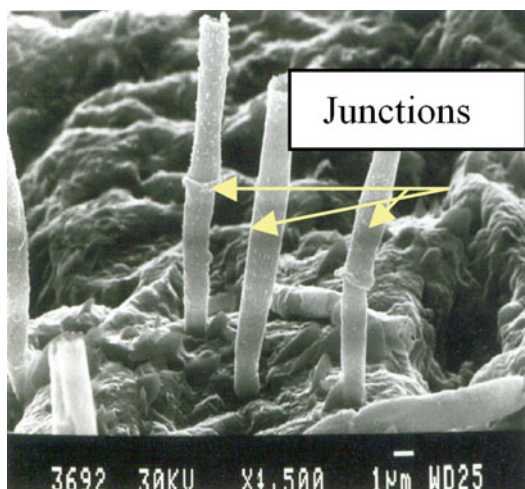
ratio as well as generation of uniform array of structures can be achieved by using AC electrodeposition. Various AC pulse shapes like saw-tooth waves, triangular, sine waves, but not



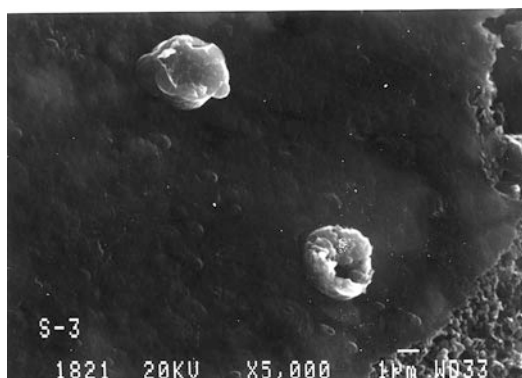
Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 10 Cu-Se nano-RTDs (Chakarvarti and Vetter 1991)



Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 12 PVDF microtubule

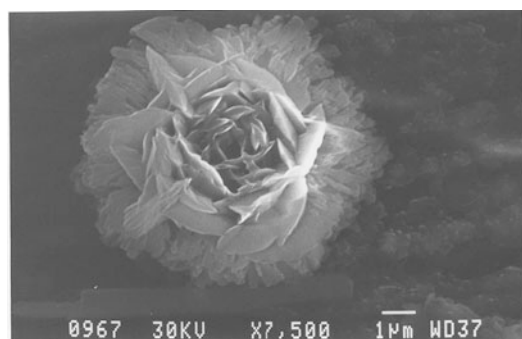


Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 11 Zn-Se nano-RTDs



Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 13 CdS microflowers (Chakarvarti et al. 2005a)

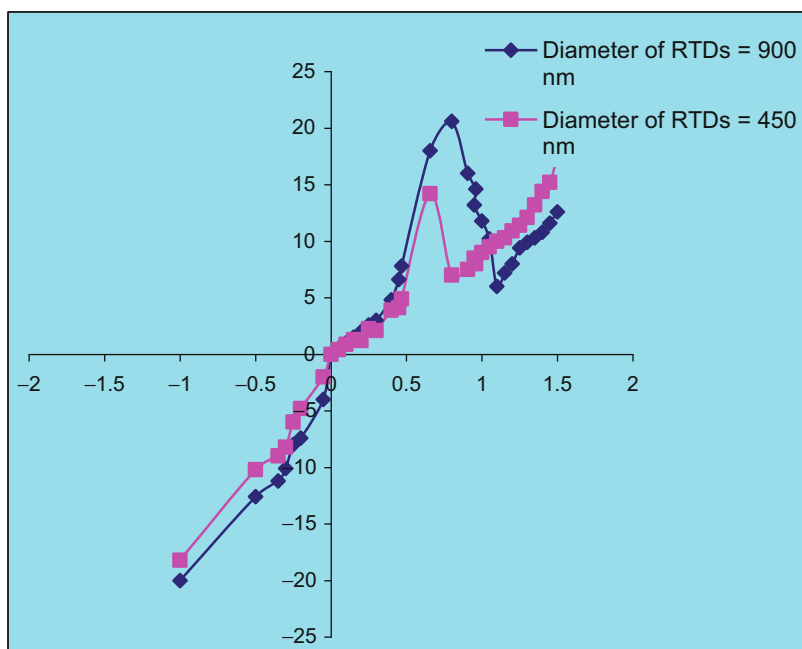
square wave (square wave potential pulses may be used for obtaining multilayered nanowires, see reference Piroux et al. (1994)) with varying frequencies have been used for better results, increased crystallinity and homogeneity (Yin et al. 2001). Nielsch et al. (2000) used pulsed electrodeposition method and demonstrated that it suits for uniform deposition of porous alumina with almost 100 % (Nielsch et al. 2000). From our experience, we have found that initial high voltage for short duration followed by low values (the



Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices, Fig. 14 Copper microrose flower

Track-Etch Membranes as Tools for Template Synthesis of Nano-/Microstructures and Devices,

Fig. 15 Collective current–voltage (I–V) characteristics of Zn-Se RTDs with average diameters of 900 nm and 450 nm



process is called “striking”) produces good results. Chakarvarti and Vetter (Chakarvarti and Vetter 1998) have suggested a formula in order to calculate an approximate optimum current for satisfactory results. It is of interest to note that the template synthesized materials (metals as well as semiconductors) in the form of solid cylinders, wires, or whiskers can be crystalline (Dobrev et al. 1994; Chakarvarti et al. 1996).

Synthesized Structures and Devices: Some Results
Some of the metallic, nonmetallic homogeneous and heterogeneous structures and devices synthesized in this lab are shown in the Figs. 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14. The template used in all cases were TEMs of Makrofol polycarbonate having pores with different shapes (some cylindrical and others conical). The Makrofol foils were got irradiated at Gesellschaft für Schwerionenforschung (GSI), Darmstadt, Germany. Also some polycarbonate foils were obtained from Whatman. More details and descriptions can be found from the references quoted.

Some of the nano-/microdevices synthesized were resonant tunneling diodes (RTDs) made from heterojunctions of metal-semiconductors

(Cu-Se, Zn-Se, Cd-Te systems, see refs. (Kumar et al. 2005, 2008a)) besides field-ion emitters (Kumar et al. 2004g, 2007b) using metallic nano/micro-tipped cylinders of copper and silver. For filling up the template pores, the electrodeposition was carried out from one face and the process was interrupted when the pores were filled half-way through. The electrolyte was replaced by another one with different metal/semiconductor material composition, and the deposition was further carried out till the pores are filled up to the brim. Figure 15 shows typical I–V characteristics of nano-RTDs synthesized from Zn-Se deposition in Makrofol PTEMs, confirming the fact that nature manifests identical both in small scale and macro scale as well. Figure 14 shows a floral display as a by-product of template synthesis process.

More results on the effect of size as well as temperature of the synthesized RTDs of II–VI materials, modeling of RTDs, and other aspects of template synthesis of variety of materials have been reported (Kumar et al. 2005, 2007a, b, c, 2008a, b, c, d, 2009, 2010a, b, 2011a, b, c, d, 2012a, b, c, d, e, 2013; Chakarvarti 2007a; Kumar and Chakarvarti 2006, 2007a, b, c, d, 2010, 2012; Chaudhri et al. 2006b, 2010;

Chaudhri and Chakarvarti 2008b, c; Chakarvarti et al. 2005b; Kaur et al. 2005, 2006, 2007a, b, c, d, 2009a, b, 2011a, b, c; Verma et al. 2005; Singh et al. 2006, 2008, 2013; Singh and Chakarvarti 2008b; Chakarvarti 2009, 2010; Sekhon et al. 2011; Gehlawat et al. 2012; Rani et al. 2013a, b).

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Traditional Diafiltration

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Traditional diafiltration (TD) is the most common type of batch diafiltration technique that accomplishes the selective separation of a macrosolute-microsolute mixture as well as the concentration of macrosolute by employing a constant-volume dilution mode step that is preceded and/or followed by concentration mode operational steps.

Due to its straightforward concept and simple configuration, TD is the most frequently used batch diafiltration technique employed in various pressure-driven membrane filtration systems including reverse osmosis, nanofiltration, ultrafiltration, and microfiltration applications. TD process normally consists of three consecutive operational steps in the following order:

1. Pre-concentration step, to increase the concentration of macrosolute up to an intermediate level
2. Constant-volume dilution step, to “wash out” microsolute by a diluant introduced into the system in order to improve the recovery of the material in the permeate or to improve the purity of the retained phase
3. Post-concentration step, to further reduce the volume and to concentrate macrosolute to the final, desired level

In certain cases, if optimality requires, the three-step TD is reduced to a two-step process with either (1) or (2) omitted from the sequence. Note that filtration in *concentration mode* removes some of the microsolute but does not reduce its concentration in the feed tank. Even in case of freely permeable microsolute (i.e.,

rejection is equal to zero), the microsolute concentration remains constant in the feed tank. Thus, concentration mode is to be coupled with constant-volume dilution mode to achieve a high level of macrosolute-microsolute separation.

The generalized process model for both concentration mode and dilution mode can be written as

$$\begin{aligned}\frac{dc_i}{dt} &= \frac{c_i q}{V} (R_i - \alpha), & c_i(0) &= c_{i0}, \\ \frac{dV}{dt} &= (\alpha - 1)q, & V(0) &= V_0\end{aligned}$$

where c_i is the solute concentration in the feed tank, R_i stands for the rejection of component i , V represents the volume in the feed tank, and α is the proportionality factor defined as the ratio of diluant flow to permeate flow q . By definition, in concentration mode, $\alpha = 0$ (i.e., no diluant is added), while in constant-volume dilution mode, $\alpha = 1$. V_0 and c_{i0} denote respectively the initial feed volume and the initial feed concentration of the solute i . This initial value problem describes the evolution in time of the feed volume and the feed concentration of any solute under the assumption that the diluant is free of component i , and the feed tank is well mixed. Note that the time-dependent variables (i.e., permeate flux and the solute rejections) are, in a general case, a function of feed concentrations and may vary with operation conditions (temperature, pressure, cross-flow velocity, etc.).

Assuming constant rejections and flux, the differential equations can be reduced to simple algebraic equations. The resulting exact solutions are:

- For concentration mode, the actual concentration of component i at any time instant gives $c_i = c_{i0} n^{R_i}$ where n is the volume concentration factor defined as the ratio of initial feed volume to actual feed volume.
- And for constant-volume dilution mode, it holds: $c_i = c_{i0} e^{D(R_i - 1)}$ where D is the dilution factor given as the ratio of applied diluant volume to feed volume.

The subject of optimization procedures is a TD process that aims at increasing the macrosolute concentration from c_{10} to c_{1f} and reducing the microsolute concentration from c_{20} to c_{2f} (e.g., Beaton and Klinkowski 1983; Dutré and Trägårdh 1994; Foley 1999; Wang et al. 2007; Paulen et al. 2012). TD is characterized with a sequence $\alpha(t) = \{0, 1, 0\}$ with two unknown switching times at the end of the first and of the second process steps. In engineering practice, process optimization is usually aimed at finding optimum values for n and D . Note that it poses a mathematically analogous problem to finding switching times. The problem of determining optimum switching times for a given technological objective has been the subject of many optimization studies, most of them considering process models with constant (i.e., concentration-independent) flux and rejections and a few dealing with concentration-dependent membrane response models (e.g., Bowen and Mohammad (1998); Kovács et al. 2008). The simplifying assumptions, when their appropriateness is not carefully checked for the given separation process, can easily result in suboptimal process control.

Optimization procedures may consider different objective functions, such as minimization of operational time, diluant consumption, or a complex economic index. This latter involves the costs of utilized diluant and pump operation and incorporates macrosolute loss-related costs. The optimal solution is case specific varying with the complexity of the permeation model (i.e., rejection and flux behavior), the initial and final values, and the constraints involved in the model.

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Transient Membrane Transport, Analysis of

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Most of the membrane processes have both transient and stationary states. Industrial or simply practical approaches neglect, wherever possible, the transient state of the process in question. There are some good reasons for that. Namely, the transient state is the first stage of a classical (or most popular) permeation process, like gas and vapor permeation, desalination, etc., but what really matters is a well-defined stationary (steady) permeation. However, the transient state is rich in the information that may be used to characterize the process and it is worth of paying an attention to (Grzywna and Petropoulos 1983a, b; Grzywna and Frisch 1984; Grzywna and Simon 1991; Fig. 1).

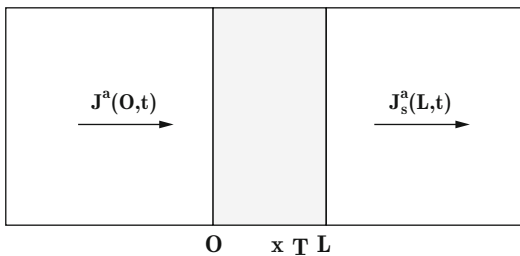
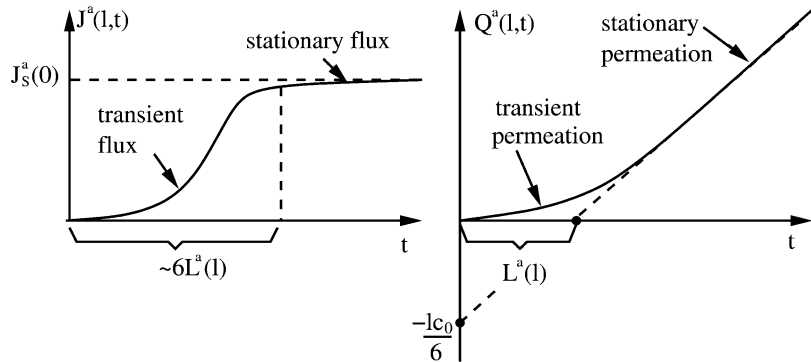
Theoretically, the relation between transient and stationary fluxes reads $\lim_{t \rightarrow \infty} J^a(l, t) = J_s^a(l)$ but practically $J^a(l, t)$ reaches its steady value after the time approximately equal to $6L^a(l)$, and then it takes the form

$$J_s^a(l, t) = \overline{D} \frac{\partial c_s(x)}{\partial x} \Big|_{x=l}$$

for the downstream side of a membrane (where $c_s(x)$ is the steady state distribution of the concentration inside of the membrane – a constant

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Fig. 1 Transient state in the mass flow and in the flux behaviour in the permeation experiment



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Fig. 2 Experimental configuration for the permeation experiment

gradient in case of an ideal Fickian diffusion). The experimental set-up is shown schematically in the figure below (Fig. 2).

The straight line on the mass plot also does not intersect the coordinate system at origin, but leaves a time lag equal to $L^a(l)$ which corresponds to the period where the concentration gradient builds up within the membrane (i.e., the supplied mass does not exit to the permeation side but becomes embedded into the membrane). This time lag can serve for the calculation of the diffusion coefficient (Frisch 1957; Strzelewicz and Grzywna 2008; Crank 1975; Simon and Grzywna 1993; Borys et al. 2013):

$$D = \frac{l^2}{6L^a(l)}$$

In addition, the vertical axis is cut in a position that allows to read the value of the boundary concentration c_0 (Fig. 1; Crank 1975,

Eq. 4.25 for $t \rightarrow 0$; Crank and Park 1968; Borys et al. 2013).

In a detailed analysis, except for the permeation curves on the exit side of the membrane ($J^a(l, t)$ and $Q^a(l, t)$) we can measure also the permeation on the feed side of the membrane, which results in curves of $J^a(0, t)$ and $Q^a(0, t)$. These curves also imprint the time lag, namely:

$$L^a(0) = 2L^a(l)$$

where $L^a(0)$ is the intercept of the mass permeation curve asymptotic line with the time axis (Rutherford 1997; Borys et al. 2013; Fig. 3).

Concluding, an analysis of a stationary state answers some simple but very practical questions. More refined problems need analysis of a transient state.

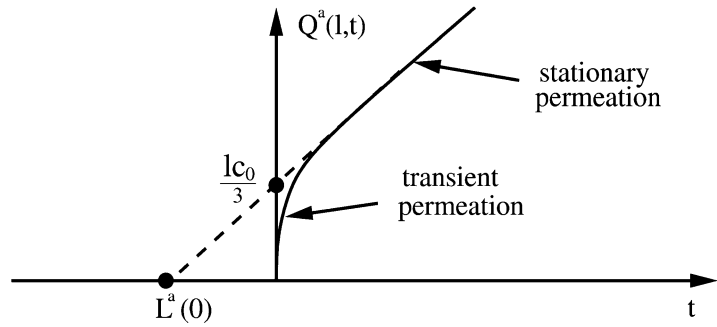
Except for the time lags, there is also another method for transient analysis of the diffusion process. It has been called the D₁-D₈ method for evaluation of the diffusion coefficients. It can be referred in form of a table of asymptotic formulas that can be fit to the permeation (or sorption) data. The formulas take the following forms (Grzywna and Petropoulos 1983; Rybak et al. 2009; Borys et al. 2013; Table 1):

In these formulas:

Q_t^a denotes the mass that is sorbed per unit surface in unsymmetrical sorption into the membrane after time t ,

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Fig. 3 Transient mass flow on the feed side in the permeation experiment



Transient Membrane Transport, Analysis of, Table 1 A collection of the asymptotic formulas for the D₁-D₈ system

Analytical formula		Notes
1	$\frac{Q_t^a}{Q_\infty} = 2\sqrt{\frac{D_1}{\pi l^2}} t^{1/2}$	Unsymmetrical sorption – early time
2	$\frac{M_t^a}{M_\infty} = 4\sqrt{\frac{D_1 M_1}{\pi l^2}} t^{1/2}$	Symmetrical sorption – early time
3	$\ln\left[1 - \frac{Q_t^a}{Q_\infty}\right] = \ln\frac{8}{\pi^2} - \frac{D_2 \pi^2}{4l^2} t$	Unsymmetrical sorption – late time
4	$\ln\left[1 - \frac{M_t^a}{M_\infty}\right] = \ln\frac{8}{\pi^2} - \frac{D_2 M \pi^2}{l^2} t$	Symmetrical sorption – late time
5	$\ln[t^{1/2} J(l, t)] = \ln\left[2c_0\left(\frac{D_4}{\pi}\right)^{1/2}\right] - \frac{l^2}{4D_3 t}$	Permeation – early time
6	$\ln[Q^a(l, t) - Q_s^a(l, t)] = \ln\frac{2lc_0}{\pi^2} - \frac{D_5 \pi^2}{l^2} t$	Permeation – late time
7	$\frac{\Delta Q_t^a}{\Delta Q_\infty^a} = 4\sqrt{\frac{D_6}{\pi l^2}} t^{1/2}$	Sorption in the permeation – early time
8	$\ln[Q_s^a(0, t) - Q^a(0, t)] = \ln\frac{2lc_0}{\pi^2} - \frac{D_7 \pi^2}{l^2} t$	Permeation – late time
9	$\ln\left[1 - \frac{\Delta Q_t^a}{\Delta Q_\infty^a}\right] = \ln\frac{8}{\pi^2} - \frac{D_8 \pi^2}{l^2} t$	Sorption in the permeation – late time

$Q_\infty = c_0 l$ denotes the mass that is sorbed per unit surface in unsymmetrical sorption into the membrane after infinitely long time,

M_t^a denotes the mass that is sorbed per unit surface in symmetrical sorption into the membrane after time t ,

$M_\infty = c_0 l$ denotes the mass that is sorbed per unit surface in symmetrical sorption into the membrane after infinitely long time,

$\Delta Q_t^a = Q^a(0, t) - Q^a(l, t)$ denotes the mass that is sorbed into the membrane per unit surface after time t during permeation,

ΔQ_∞ denotes the mass that is sorbed into the membrane per unit surface during permeation after infinitely long time (in case of Fickian diffusion it is $\Delta Q_\infty = c_0 \frac{l}{2}$),

$J(l, t)$ denotes the flux on the exit side of the membrane,

$Q^a(l, t)$ denotes the mass that has permeated per unit surface to the exit side of the membrane,

$Q_s^a(l, t)$ denotes the asymptotic straight line curve of the mass per unit surface on the exit side,

$Q^a(0, t)$ denotes the mass that has permeated per unit surface to the feed side of the membrane,

$Q_s^a(0, t)$ denotes the asymptotic straight line curve of the mass per unit surface on the feed side,

c_0 is the feed concentration,

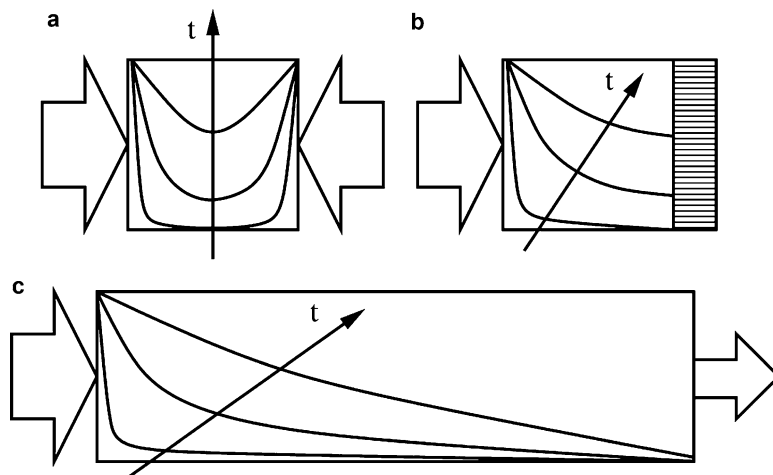
$D_1 \div D_8$ are the diffusion coefficients (equal to D in the ideal Fickian case),

t is the time.

The drawings in Fig. 4 explain the experimental set-ups and show the considered fluxes and concentration profiles within the membrane. Case (a) depicts the symmetrical sorption, case (b) depicts the unsymmetrical sorption, and case

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Fig. 4 Experimental setups for transient membrane transport analysis and the corresponding fluxes together with concentration profiles; (a) symmetrical sorption, (b) unsymmetrical sorption, (c) permeation



(c) depicts permeation. In case of “sorption in the permeation” (based on the set-up (c)), the sorbed mass is just the integral of the concentration profile with respect to length, multiplied by the membrane surface (Fig. 4).

It is important to note the meaning of different diffusion coefficients in the above table of equations. All of these formulas are derived from the solution of a simple second Fick’s law (see the supplementary materials of Borys et al. 2013), and for simple diffusion they all have the same value, i.e., $D_1 = D_2 = \dots = D_8 = \bar{D}$. This is however no longer the case when the diffusion is non-Fickian. For example in concentration-dependent diffusion D_2 (measured mostly in the state of a terminal concentration) will provide an estimate of $D(c_{max})$ while D_1 will only provide a sort of an average of the concentration dependency. The work (Crank and Park 1968, p. 18) provides an estimate of such an average diffusion coefficient by:

$$\bar{D} = p c_0^{-p} \int (c - c_0)^{p-1} D(c) dc$$

where p should be equal to 1.67 for an increasing concentration dependency of the diffusion coefficient in sorption and 1.85 for a decreasing dependency. The raw formula, with $p = 1$ was established exactly for the stationary permeation experiment.

All of the above asymptotic formulas are presented in form of an equation $y = ax + b$,

suitable for a linear regression. For example, in the permeation experiment we can make use of equation 5 from the table and then $y = \ln[t^{1/2}J(l, t)]$, $x = \frac{1}{t}$, $a = \frac{-l^2}{4D_3}$, $b = \ln\left[2c_0\left(\frac{D_3}{\pi}\right)^{1/2}\right]$. The linear regression clearly allows to determine the constants a and b , and as a consequence the diffusion coefficients, denoted D_3 and D_4 .

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Transparent Exopolymer Particle

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Introduction

Transparent exopolymer particles (TEPs) refer to a variety of biopolymers or exopolymeric substances (EPS) in aquatic systems which can be identified by Alcian blue staining. TEPs were first described in 1993 by Alice Alldredge and coworkers (1993) shortly after discovering these materials by staining with Alcian blue dye – a cationic dye known to specifically complex with anionic groups of polysaccharides and glycoprotein (Ramus 1977). As the name suggests, TEPs are transparent organic substances seasonally abundant (e.g., algal bloom) in marine, brackish, and nonsaline surface waters (Passow 2002a; Emery et al. 1984). These substances mostly originate from exudates of phytoplankton and bacterioplankton but may also originate from macroalgae, oysters, mussels, scallops, and sea snails (Passow 2002b; McKee et al. 2005; Heinonen et al. 2007; Thornton 2004). They consist of hydrophilic, negatively charged, and mostly surface-active acidic polysaccharides containing mostly half-ester sulfate (R-OSO_3^-) and to the lesser extent carboxyl (R-COO^-) functional groups (Mopper

et al. 1995; Zhou et al. 1998). TEP has been reported to be in various forms (e.g., strings, disks, sheets, or fibers) and sizes, ranging from 3 nm in diameter up to 100 s of μm long (Berman and Holenberg 2005; Passow 2000).

For the last two decades, the presence of transparent exopolymer particles (TEPs) in seawater and freshwater and their important role in the carbon cycle in aquatic systems have been extensively studied in the field of oceanography and limnology (see review by Passow 2002a). However, their significance to membrane-based water treatment technologies has only been investigated recently. Berman and Holenberg (2005) proposed monitoring TEP in desalination plants after it was implicated as a potential cause of fouling in membrane systems. Consequently, a number of studies were conducted to investigate their presence in feedwater sources and their possible link to membrane fouling (Bar-Zeev et al. 2009; Villacorte et al. 2009a, b, 2010a, b). Moreover, the presence of TEP has also been reported in wastewater sources of membrane systems (de la Torre et al. 2008; Kennedy et al. 2009).

Identification and Measurement

Although TEP has only been known for about 20 years, the presence of transparent microscopic marine substances detectable only by staining and electron microscope had been reported way back in the 1970s (Gordon 1970; Winters et al. 1983). However, the transparent character of TEP complicated earlier studies to investigate their abundance in aquatic systems. Currently, TEP has been roughly defined as particles, recognizing that the first method used 0.4 micrometer polycarbonate membranes to extract them from the water (Alldredge et al. 1993). However, the current understanding about TEP has been changing through the years. TEPs are not real particles, as its name suggests, but rather aggregates of hydrogels which are highly deformable and can vary in size from few nanometers to hundreds of micrometers (Passow 2002a, b; Verdugo et al. 2004). Majority of these substances were formed abiotically from colloidal precursors by

spontaneous assembly of colloidal polymers in surface water (Chin et al. 1998; Passow 2000). Moreover, monitoring TEP in membrane treatment plants proved to be a challenge because MF/UF membranes can theoretically reject these materials if measured with 0.4 micrometer pore size membranes but will not totally reject their colloidal precursors which might spontaneously assemble into measurable TEP downstream. Therefore, it is increasingly important to incorporate this colloidal fraction in the TEP measurements in order to sufficiently assess the rejection by pretreatment systems. The use of liquid chromatography-organic carbon detection (LC-OCD) is a promising technique to estimate the presence of these of colloidal fraction in aquatic systems (Villacorte 2009a, b, 2010a, b; Amy et al. 2011).

Currently, there are four established methods to measure TEP. These methods either involve direct counting (Alldredge et al. 1993) or spectrophotometric measurements (Passow and Alldredge 1995; Arruda-Fatibello et al. 2004; Thornton et al. 2007), all of which involve Alcian blue staining. The spectrophotometric assay developed by Passow and Alldredge (1995) is currently the most widely used and accepted method to measure TEP. In this method, TEPs were collected through vacuum filtration on polycarbonate membrane filters (0.4 μm pore size), stained with Alcian blue, and dissolved in sulfuric acid, and then the absorbance Alcian blue bound to TEP was measured spectrophotometrically at 787 nm wavelength. Those biopolymers which passed through the filters are considered as TEP precursors or colloidal TEP ($<0.4 \mu\text{m}$; Passow 2000).

Potential Impact on Membrane Filtration and Control

TEPs comprise surface-active materials (e.g., half-ester sulfate groups) which is the main ingredient of their high stickiness (Mopper et al. 1995; Zhou et al. 1998; Dam and Drapeau 1995; Engel 2000). The relative stickiness of TEP is estimated to be between two and four orders of magnitude

higher than most other suspended particulates in surface water (Passow 2002a). TEPs may also form large gel-like materials which may function like a sponge capable of absorbing/retaining nutrients and trace elements from surface water, making them a nutritious platform and a good refuge for bacteria to grow and multiply (Alldredge et al. 1993; Berman and Holenberg 2005). Moreover, TEPs can be direct alternative carbon nutrient for bacteria as they are partially biodegradable (Passow 2002a). Based on these characteristics, Berman and company (Berman and Holenberg 2005; Berman 2010; Berman et al. 2011; Bar-Zeev et al. 2012) introduced the concept of TEP as a major initiator of biofilm development in reverse osmosis (RO) membranes. Initially, the sticky TEP material may accumulate on RO membranes (including feed spacers) and create a conditioning film conducive for bacterial attachment. Once the bacteria are attached to the film, they can effectively utilize the available dissolved nutrients (C, P, N) in the feedwater and eventually grow into large colonies. If nutrients are not limited in the system, the initial TEP layer gradually transforms into a biofilm as colonies of attached bacteria start to produce more exopolymeric substances in addition to the further accumulation of TEP from the feedwater. Current anti-biofouling strategies are usually designed to limit the influx of nutrients to the RO system by pretreatment or by applying a biocide to control bacterial population. Hence, limiting biological activity in the system may not be enough to prevent organic fouling, considering that TEP may still accumulate on the RO membrane if the pretreatment systems are not sufficiently removing them.

Although initially TEPs were only implicated as a potential problem in cross-flow NF/RO membrane systems, they are likely a major problem in dead-end membrane filtration systems (MF/UF), especially during algal blooms. With their macromolecular size (up to hundreds of micrometers), TEP can be largely (if not totally) rejected during membrane filtration. TEP may serve as a binding agent of rejected materials (e.g., particles and other organic substances) that can accumulate on membrane surfaces. Since TEPs are negatively

charged and surface-active substances, they have the high tendency to adhere to membrane surfaces than other foulants. Additionally, abundant divalent ions (e.g., Ca^{2+}) in surface water can enhance gelation of TEP by cationic bridge formation (Passow 2002). With the binding and aggregation capability of TEP, it can enhance accumulation of a cake layer on the membrane with higher hydraulic resistance and lower backwashability than other suspended materials (including algal cells). This scenario has been demonstrated in recent studies of a pilot plant treating seawater impacted by algal bloom which generated high concentrations of TEP (Schurer et al. 2012; Villacorte et al. 2010a, b). In these studies, it was also found that inline coagulation can be an effective pretreatment technique to minimize fouling of MF/UF membranes during filtration of surface of water with high concentrations of TEP.

Cross-References

- ▶ [Extracellular Polymeric Substance \(EPS\)](#)
- ▶ [Liquid Chromatography: Organic Carbon Detection \(LC-OCD\)](#)

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Transport Mechanisms with Liquid Membranes

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The commonly accepted mechanism for the transport of a solute in liquid membrane (LM) is

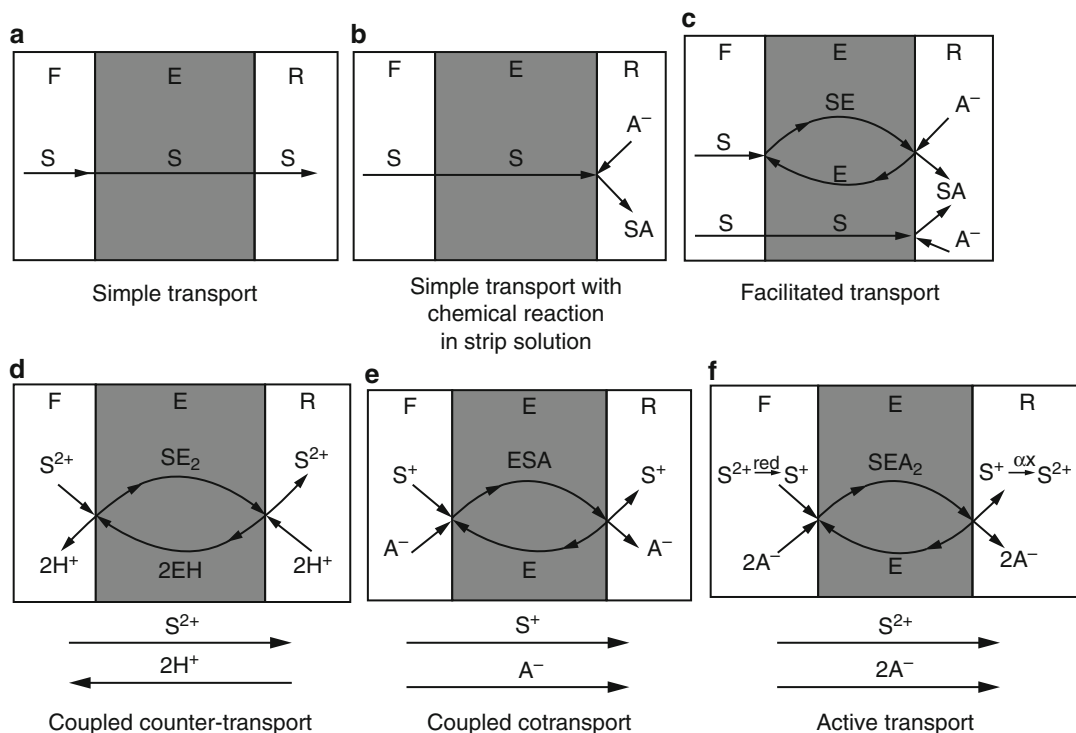
solution-diffusion. The solute species dissolve in the liquid membrane and diffuse across the LM due to an imposed concentration gradient. Different solutes have different solubilities and diffusion coefficients in LM. According to the transport mechanisms, the LM techniques may be divided into six basic mechanisms of transport, schematically shown in Fig. 1.

In a simple transport (Fig. 1a), solute passes through due to its solubility in LM. Permeation stops when concentration equilibrium is reached. The solute does not react chemically with LM and is supposed to be in the same form in the feed (F), LM (E), and receiving, R, phases. As an example, some carboxylic and amino acids, phenol transport through xylene, decanol LM may be presented. Uphill transport and selectivity in the simple mechanism can be achieved at reaction of the solute with components of the stripping solution (see Fig. 1b). Some authors relate this technique to the facilitated transport.

The efficiency and selectivity of transport across the LM may be markedly enhanced by the presence of a mobile complexation agent (carrier) in the liquid membrane. This process is known as facilitated or carrier-mediated liquid membrane separation. The transport can be described by subsequent partitioning, complexation, and diffusion. The complex reverse reacts on the LM-receiving side interface releasing the solute which partitioning to the receiving (strip) phase (see Fig. 1c). Carriers for the selective transport of neutral molecules, anions, cations, or zwitterionic species have undergone intensive development in the last two decades.

In many cases, the facilitated transport is combined with coupling counter- or cotransport (see Fig. 1d, e) of different ions through LM. The coupling effect supplies the energy for uphill transport of the solute. Facilitated transport is markedly enhanced by the efficiency and selectivity of transport across the LM.

Active transport (see Fig. 1f) is driven by oxidation-reduction, catalytic reactions, and biochemical conversions on the membrane interfaces. As a rule, it is highly selective: no other species are transported at this type of transport. In many cases, chemical reactions in LM are



Transport Mechanisms with Liquid Membranes, Fig. 1 Schematic mechanisms of solute transport through the liquid membranes. *S* is solute to be separated, *A* are

anions cotransported, *E* is liquid membrane, *F* is feed solution, *R* is stripping solution, *red* is reduction, *ox* is oxidation

irreversible in active transport. As examples, copper transport by thioether and picrate anions by ferrocene as carriers may be presented.

The rates of chemical changes and/or rates of diffusion may control all liquid membrane transport kinetics. At least one of the chemical or diffusion steps is slow enough to control the rate of the overall transport. So, analysis of mechanisms and kinetics of the chemical and diffusion steps of the overall LM transport system is needed to find the rate-controlling ones. A universal model for all these types of transport does not exist, and the available knowledge concerning the specific interfacial processes should be taken into account in the description of real membrane process.

The basic idea of the chemical kinetics-diffusion method is that the solute presented in the different phases is considered as different chemical species obeying the laws of chemical kinetics. The general assumptions of the transport

may be formulated as: (1) Steady-state conditions of the solute transport through the phase interfaces: all fluxes are necessarily the same. (2) The overall mass-transfer rate of solute can be controlled by any of the chemical reaction-diffusion resistances in the liquid phases. (3) The overall mass-transfer resistance at steady state is the sum of individual mass-transfer resistances at diffusional regime through the boundary films and chemical reactions resistances at the phases' interface. (4) Membrane supports have uniform pore size and wetting characteristics throughout membrane. Hydrophobic membrane pore is completely wetted by organic phase; hydrophilic or ion-exchange membrane pore is completely filled with aqueous phase. (5) Thermodynamic local equilibrium at the uptake (feed-LM) and release (LM-strip) interfaces. (6) The aqueous or organic stagnant boundary films diffusion resistances may be combined with the diffusion resistances of the same liquid films (aqueous or organic) inside the

membrane pores (taking into account the membrane porosity and tortuosity) in one-dimensional series of diffusion resistances.

In all configurations (BLM, SLM, ELM) we have: (1) diffusion steps in aqueous feed and strip stagnant boundary layers, (2) diffusion of the complex solute-carrier in the LM phase and/or interdiffusion (diffusion in the filled membrane support pores), (3) partitions between aqueous feed and organic LM phases at feed-LM interface (forward extraction) and between LM and aqueous strip phases at LM-strip interface (backward extraction), and (4) kinetics of chemical interactions with formation of solute-carrier complex (complexation) and destruction of complex (decomplexation). All these steps have mathematical descriptions. (For details see BLM, SLM, and ELM entries and Kislik 2010).

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Treating Pomegranate Juice, Application of Membrane Processing

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Pomegranate (*Punica granatum* L., Punicaceae) is one of the most nutritious fruits which is grown in the Middle East. Pomegranate juice in its original state has a turbid appearance which makes it difficult to preserve and undergo additional processes. Microfiltration and ultrafiltration are two pressure-driven processes which are used to clarify fruit juices.

Ultrafiltration decreases the turbidity of pomegranate juice at the same content as microfiltration

process. Other physicochemical characteristics of pomegranate juice such as acidity, total anthocyanin content, total phenolic component, antioxidant activity, and total soluble solid content similarly decrease in both ultrafiltration and microfiltration. However, microfiltration has more permeate volume than ultrafiltration which introduces it as a preferred process. On the other hand, pretreatment of pomegranate juice with microfiltration can largely increase the volume of clarified juice (Mirsaedghazi et al. 2012). Also, physicochemical characteristics of pomegranate juice are similarly changed in process using mixed cellulose ester membrane with pore sizes of 0.22 and 0.45 μm and hydrophilic polyvinylidene fluoride membrane with pore sizes of 0.22 and 0.45 μm . Evaluation of the five major anthocyanins in pomegranate juice including cyanidin 3-glucoside, cyanidin 3,5 diglucoside, delphinidin 3-glucoside, pelargonidin 3-glucoside, and pelargonidin 3,5-diglucoside and ellagic acid showed that all of them decreased after clarification with all membranes (Mirsaedghazi et al. 2010b).

Evaluation of the effect of process characteristics on permeate flux showed that the permeate flux raises with increasing membrane hydrophilic property. So, mixed cellulose ester membrane has more permeate flux than polyvinylidene fluoride one. Also, larger membrane pore size produces more clarified pomegranate juice. On the other hand, more transmembrane pressure makes more permeate flux especially in the first stages of membrane processing. However, difference between permeate flux in various transmembrane pressures is removed at the last stages of membrane processing to make a cake layer which acts as a secondary membrane. Also, rising of feed velocity increases permeate flux in all stages of clarification processing due to decrease cake layer thickness (Mirsaedghazi et al. 2010a, 2009b).

Evaluation of the fouling phenomenon in microfiltration of pomegranate juice showed that the cake formation is induced in the first stages of membrane processing and it follows by the intermediate blocking, the standard blocking, and the complete blocking, respectively. Also, cake formation was dominant mechanism of fouling in

membrane clarification of pomegranate juice (Mirsaeedghazi et al. 2009a).

Another application of membrane processing to treat pomegranate juice is concentration of juice using osmotic distillation and membrane distillation. Osmotic distillation can concentrate pomegranate juice 3.2 times. However, its antioxidant property does not change due to constant level of anthocyanins and phenol component of pomegranate juice (Cassano et al. 2011). Another research showed that osmotic distillation can increase total soluble solids of pomegranate juice from 17 to 55° Brix after about 400 min. Coupled osmotic distillation and membrane distillation can similarly concentrate pomegranate juice at 250 min. Researchers concluded that membrane processing can change parameters of pomegranate juice such as pH, total titratable acidity, color characteristics, total antioxidant activity, total phenolic content, total monomeric anthocyanins, individual phenolics, and organic acid composition. However, thermal treatment reduces such parameters in pomegranate juice (Onsekizoglu 2013).

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Tricaprylamine

► [Alamine 336](#)

Tridioctylamine

► [Alamine 336](#)

Tri-*n*-caprylamine

► [Alamine 336](#)

Tri-*n*-octylamine

► [Alamine 336](#)

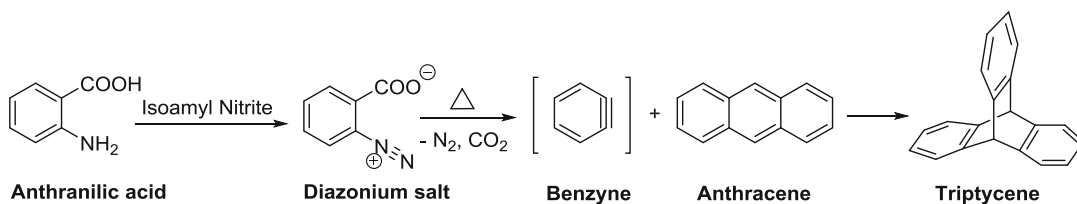
Trioctylamine

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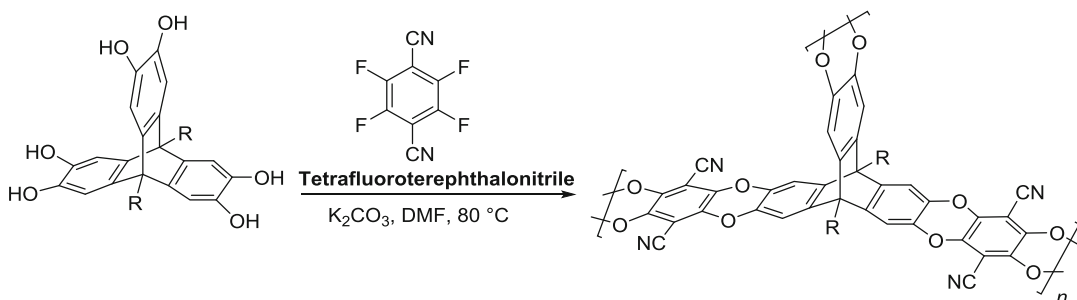
Triptycene Polymer with Intrinsic Microporosity

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Triptycene and its derivatives are a class of interesting aromatic compounds with unique, concave, three-dimensional frameworks. Because of the



Triptycene Polymer with Intrinsic Microporosity, Fig. 1 Formation of the triptycene core



Triptycene Polymer with Intrinsic Microporosity, Fig. 2 Synthesis of triptycene network PIMs. R = H, Me, Et, Pr, 'Pr, Bu, 'Bu, Pent, Oct, Bz

almost perfectly trigonal shape they have been used for several different applications in the field of material chemistry. Typically the synthesis of triptycene-based compounds starts from the formation of the very reactive benzyne intermediate, for example, from the anthranilic acid, which can easily undergo Diels-Alder reaction with anthracene to form the triptycene core as shown in Fig. 1.

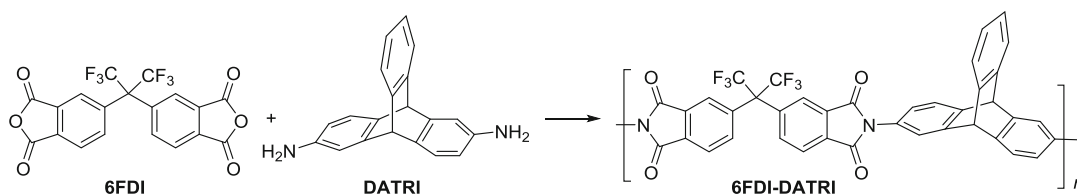
Probably the most important characteristic of the triptycene framework comes from the rigidity of its propeller-like structure and the guarded space between the aromatic faces which has been defined as “Internal Molecular Free Volume” (Long and Swager 2001). In fact, when functionalized triptycenes are used to form polymers, their packing in the solid state becomes very inefficient so that local cavities are created, leading to the formation of a highly microporous material. There is a great variety of examples of the use of this interesting building block for the synthesis of highly microporous materials. For instance, hexa-amino (Kohl et al. 2014) or hydroxo-based triptycenes (Taylor et al. 2014) were used to synthesize discrete molecules with

elevated microporosity. Kahveci et al. reported the use of triptycene-based molecules to make very high surface area (up to $3,800 \text{ m}^2 \text{ g}^{-1}$) covalent organic frameworks (COFs), exploiting the trigonal shape of the triptycene to form very well-defined hexagonal channels. They demonstrated the possibility of using these materials for elevated absorption of CH_4 and CO_2 at 273 K (Kahveci et al. 2013).

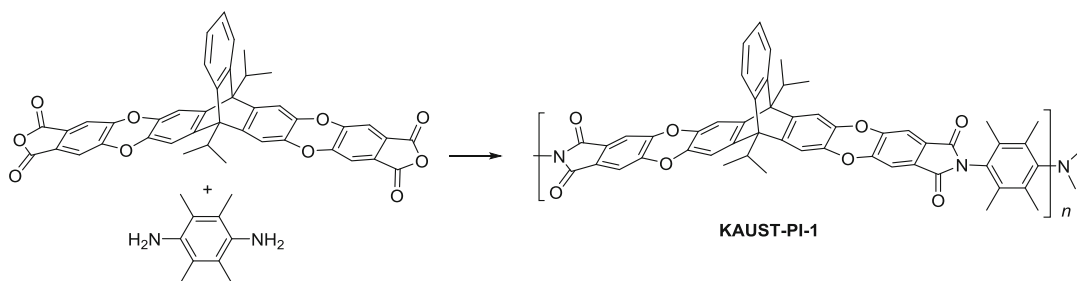
A series of triptycene-based network polymers of intrinsic microporosity (PIMs), reported in 2010 (Fig. 2; Ghanem et al. 2010), showed the ability of functionalized triptycenes to be used for selective gas adsorption. These networked PIMs were built from hydroxyl-substituted triptycene units with varying lengths of alkyl chains attached to the bridgehead position (R).

When polymerized with tetrafluoroterephthalonitrile via nucleophilic aromatic substitution, these monomers afforded polymers whose BET surface area varied according to the length of the alkyl chain of the bridgehead, proving the versatility of the functionalized triptycenes.

It was found that short alkyl chains (H, Me, Et, Pr) lead to highly porous materials with the



Triptycene Polymer with Intrinsic Microporosity, Fig. 3 Synthesis of 6FDI-DATRI polyimide



Triptycene Polymer with Intrinsic Microporosity, Fig. 4 Synthesis of KAUST-PI-1

highest BET surface area of $1,760 \text{ m}^2 \text{ g}^{-1}$ when $R = \text{Me}$, whereas increasing the length of the alkyl chains caused a decrease in surface area due to an elevated fraction of the generated free volume becoming occupied by the flexible side chains.

Because of the high rigidity of the bridged poly-aromatic ring, which often limits the solubility of the obtained material, there are not many examples of triptycene-based polymers that formed robust solution-processable membranes to be used for gas separation.

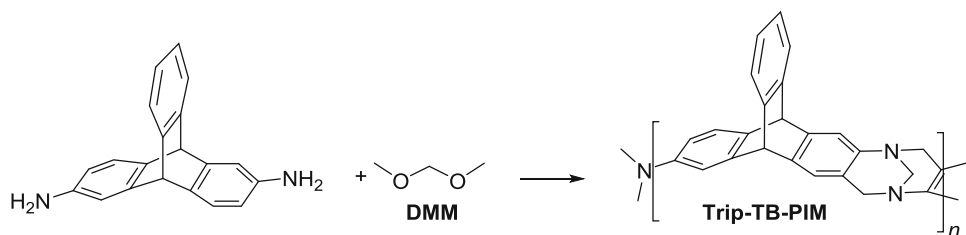
In the past few years, though, there have been new progresses in this field which led to the synthesis of high-performing triptycene-based materials with excellent performance for gas separation.

In 2011, Park and Cho realized a polyimide containing a diamino triptycene linked with the commercial hexafluoro dianhydride (6FDA, Fig. 3), which is one of the most used monomers for the formation of high-performance polyimides for gas separation (Cho and Park 2011). The free rotation around the imide linkage provided a low surface area (only $68 \text{ m}^2 \text{ g}^{-1}$), which limits the mass transport of the gasses into the membrane and, consequently, the permeability. Despite the low permeability, the excellent selectivities

demonstrated by this polymer allowed it to surpass the Robeson upper bound for important gas pairs such as O_2/N_2 and CO_2/CH_4 .

In order to increase the free volume, Pinnau et al. used a similar approach synthesizing an extended triptycene dianhydride with bulky isopropyl substituents on the bridgehead, polymerizing it with the commercial tetramethyl phenylenediamine. The combination of the rigidity of the bulky triptycene and the hindrance of the four methyl groups of the phenylenediamine, which restricts the rotation around the imide linkage, afforded a polyimide with very high BET surface area (KAUST-PI-1, $750 \text{ m}^2 \text{ g}^{-1}$, Fig. 4). The increase of the free volume led to high permeability which, in combination with decent selectivities, allowed them to obtain a high-performing material for gas separation (Ghanem et al. 2014).

A different method was followed by the McKeown group for the synthesis of highly porous and permeable triptycene-based polymers of intrinsic microporosity synthesized via Tröger's base polymerization (Trip-TB-PIM, Carta et al. 2014). By using a diamino triptycene and reacting it with an excess of dimethoxymethane (DMM), they obtained a polymer which combines the high rigidity of both



Triptycene Polymer with Intrinsic Microporosity, Fig. 5 Triptycene-based Trip-TB-PIM

triptycene and Tröger's base (TB) cores. The contribution of the two rigid frameworks afforded a highly microporous polymer (Trip-TB-PIM, $900 \text{ m}^2 \text{ g}^{-1}$, Fig. 5). Despite the increased stiffness of the backbone, the material resulted soluble in common solvent from which it was casted a robust self-standing thin film membrane. The combination of high surface area, which boosted the permeability, and the polarity of the TB core that enhanced the selectivities for important gas pairs allowed this triptycene-based polymer to go well beyond the Robeson upper bound for H_2/N_2 , O_2/N_2 , and CO_2/CH_4 .

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Tubular Membrane

► Tubular Membrane Module

Tubular Membrane Module

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Synonyms

[Tubular membrane](#); [Tubular module](#)

A tubular membrane module is based on tubular membranes which have the same membrane geometry as capillary membranes and hollow fiber membranes but different dimensions. Tubular membranes have an outer diameter which ranges from 5 to 25 mm (Scholz et al. 2011).

In contrast to capillaries and hollow fibers, tubular membranes are not self-supporting. Such membranes are placed inside a porous stainless steel, ceramic, or plastic tube with the diameter of the tube being, in general, more than 10 mm. The number of tubes put together in the module may

vary from 4 to 18, but is not limited to this number (Mulder 1997).

The feed solution always flows through the center of the tubes, while the permeate flows through the porous supporting tube into the module housing. Ceramic membranes are mostly assembled in such tubular module configurations. However, the packing density of the tubular module is rather low, being less than $300 \text{ m}^2/\text{m}^3$ (Mulder 1997).

Tubular modules are nowadays generally limited to ultrafiltration applications where the higher resistance against membrane fouling as an effect of the good fluid hydrodynamics outweighs the high costs (Baker 2004).

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Tubular Module

► Tubular Membrane Module

Turndown in Gas Separation

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Turndown is the capability of the system to operate at reduced capacity (Miller and Söcker 1989). In gas separation, membrane systems are highly capable of maintaining product purity even

though the capacity is reduced down to 10 % of the initial design. This is done by either reducing feed pressure, increasing permeate pressure, or by isolating modules from the system. The first two methods can be used for short-term operation and the latter when operating at significantly reduced capacity for extended periods. No provisions are required in the design phase.

Absorption units can maintain both recovery and product purity at throughputs of ca. 30–100 % of design by adjustment of the gas streams and solvent flow rates.

Also PSA units can maintain both recovery and product purity at throughputs of ca. 30–100 % of design by adjustment of the cycle time. Between 0 % and 30 % of design product rates, purity can be maintained, but recovery is reduced unless special provisions are made in the design.

The turndown capability of cryogenic systems strongly depends on the design. Partial condensation units can maintain product purity at slightly reduced recovery at flows down to 30–50 % of design.

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Two-Dimensional Amphiphilic Aggregates

► Amphiphilic Membrane

Two-Separate Phase Biocatalytic Membrane Reactors

► Biphasic Biocatalytic Membrane Reactors

U

UF Membranes (Ultrafiltration Membranes)

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UF membranes are thin porous solids that perform separations by retaining and passing solutes primarily based on their size. Key membrane properties include retention capability, solvent permeability, chemical compatibility, mechanical strength for module fabrication and repeated use, consistency, and cost. They have nominal molecular weight limit (NMWL) ratings of 1–5,000 kDa to retain solutes such as macromolecules, nanoparticles, and colloids while passing smaller solutes and solvents. UF membranes retain smaller solutes than microfiltration membranes and larger solutes than reverse osmosis membranes. Food and medical applications require extractable testing, adsorption, shedding, and United States Pharmacopeia (USP) class VI toxicity testing. In addition, these applications require high consistency membranes with vendor quality programs (e.g., International Organization for Standardization (ISO), current good manufacturing practices (cGMP)). With reuse, membrane cost is significantly reduced.

UF membranes primarily consist of polymers (polyethersulfone, regenerated cellulose, polysulfone, polyamide, polyacrylonitrile, or various

fluoropolymers) formed by immersion casting on a web or as a composite cast on an MF membrane. A multicomponent, high polymer concentration (5–25 %) viscous solution (lacquer) is well mixed, degassed, and filtered to remove particles or trap air. The lacquer contains a nonsolvent which separates into droplets and becomes the pores of the UF membrane. Hollow fibers are formed by metering the lacquer through a die into an immersion bath. Flat sheet membrane is formed by metering the lacquer through a precisely controlled slot to coat a support web lying on a casting drum. Early UF immersion cast membranes cast on a solid web had thin surface retentive layers with an open structure underneath. These membranes were prone to defects and showed poor retention and consistency. Newer composite membranes use a MF membrane as the support web with the UF layer cast on top. These composites demonstrate consistently high retention and can be integrity tested using air diffusion in water.

The web coat or extruded fiber is fed into an immersion liquid bath that causes the lacquer solvent to diffuse out of the lacquer coat (desolvation). Then solubility limits are reached (demixing) where the nonsolvent phase nucleates and grows (spinodal decomposition) and the solid polymer phase nucleates and grows (gelation). The polymer structure then coalesces into its final structure (phase transformation). The membrane structure is formed rapidly at nonequilibrium conditions, but the trajectory is

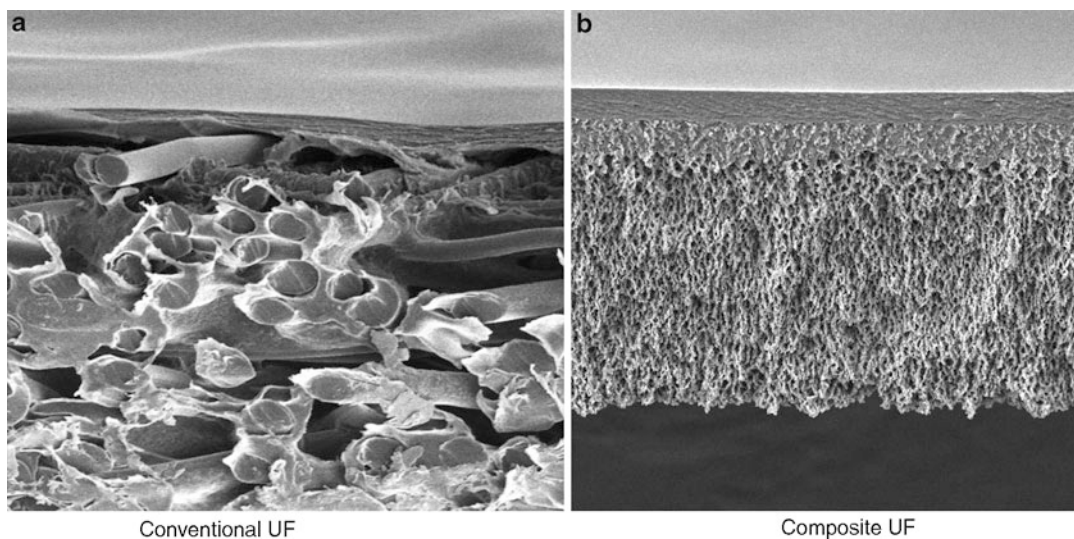
UF Membranes (Ultrafiltration Membranes), Table 1 UF membranes

Material	Advantages	Disadvantages
Polyethersulfone (PES)	Resistance to temperature, Cl ₂ , pH, easy fabrication	Hydrophobic
Regenerated cellulose	Hydrophilic, low fouling	Sensitive to temperature, pH, Cl ₂ , microbial attack, mechanical creep
Polyamide		Sensitive to Cl ₂ , microbial attack
Polyvinylidene fluoride (PVDF)	Resistance to temperature, Cl ₂ , easy fabrication	Hydrophobic, coating sensitive to high pH
Inorganic	Resistance to temperature, Cl ₂ , pH, high pressure, solvents, long life	Cost, brittleness, high cross-flow rates

commonly plotted on a ternary phase diagram. Foam or nodular structures form depending on the formation path. Asymmetry or skin structures can form depending on the kinetics of diffusive transport and nucleation. The key control parameters are the composition of the lacquer, composition of the immersion bath, coating or extrusion thickness, casting speed, bath temperature, and bath flow velocity.

Residual solvent and anti-solvent are washed out of the polymeric membrane structure in separate extraction baths. Hydrophobic polymers are surface modified to render them hydrophilic and thereby reduce fouling, reduce product losses, and increase flux.

Inorganic UF membranes (alumina, glass, and zirconia) are formed by sintering. Layers of spherical particles are deposited on a substrate and heated to fuse them together. Pores are formed in the gaps between the spherical particles. Successive layers of smaller and smaller particles can be deposited to make tighter membranes. These membranes find use in corrosive applications where their high cost can be justified (Table 1, Fig. 1).



UF Membranes (Ultrafiltration Membranes), Fig. 1 Regenerated cellulose ultrafiltration membrane side view SEM. (a) Conventional UF, (b) Composite UF (Courtesy of Millipore Corporation)

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UF Modeling (Ultrafiltration Modeling)

Herb Lutz

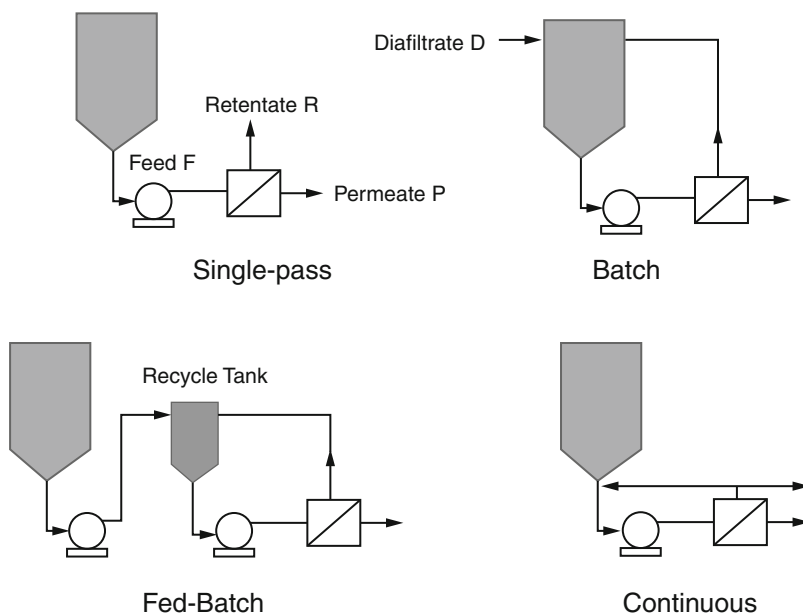
EMD Millipore Corporation, Playa del Rey, CA, USA

Basic membrane process configurations include single-pass, batch, fed-batch, and continuous operation (Fig. 1). Single-pass operation involves a single pass of feed through the module feed channel where it exists as sufficiently concentrated retentate. This requires a long residence time in the modules using long feed channels and/or low feed flow rates. Component concentrations change along the length of the retentate channel. Analysis starts with the steady-state component and solvent mass balances as shown in the Table 1. These consider an incremental area

element, dA , in the axial or flow direction for a feed channel, module, or membrane assembly of constant width. Constant density is also assumed. Combining the balance equations and integrating yields a relation between concentrations, volume reduction, and solute passage. The area required for processing is obtained by integrating the solvent balance. The Cheryan flux approximation $\bar{J} = 0.33J_{\text{initial}} + 0.67J_{\text{final}}$ is useful. Flux decreases along the feed channel due to a reduction in pressure by friction, a reduction in crossflow due to permeate losses, and an increase in osmotic pressure due to concentration increases in the retained solute. Eventually, conditions in the feed channel reach an osmotic pinch point where there is no net driving force for the flow. Beyond this point, the flow may run in a reverse direction. To solve for details of the flow, one needs an appropriate flux model relating flux to cross flow, concentration, and pressure and a hydraulic model showing how retentate pressure profiles vary with flow for feed spacer-filled channels. One can use simplified linear or gel flux models as an approximation.

Continuous operation (also called feed and bleed) is similar to single-pass operation but

UF Modeling (Ultrafiltration Modeling), Fig. 1 UF Modeling



UF Modeling (Ultrafiltration Modeling), Table 1 UF Modeling

	Single pass	Batch concentration and diafiltration	Fed-batch concentration	Continuous (feed and bleed) concentration and diafiltration
Solvent balance	$\frac{dR}{dt} = -J$	$\frac{dV}{dt} = -JA - D$	$\frac{dV}{dt} = -J$	$F_n + D_n = R_n + P_n$ per stage n
Component balance	$\frac{dM_i}{dA} = -JC_iS_i$	$\frac{dM_i}{dt} = -JAC_iS_i$	$\frac{dM_i}{dt} = -JAC_iS_i$	$F_nC_{in-1} = R_nC_{in} + P_nC_{in}S_{in}$ per stage n
Volume reduction factor X =	$\frac{F-R}{J}$	F/R	F/R	F_n/R_n per stage n
Retentate concentration C_i =	$C_{i0}X^{(1-S_i)}$	$C_{i0}X^{(1-S_i)}e^{-S_iN}$	$[C_{i0}/S_i] \left[1 - (1 - S_i)e^{-S_i\tau(1-\frac{1}{X})} \right]$	$C_{in-1} \{ X_n / [1 - S_{in} + S_{in}X_n(1 + N_n)] \}$ per stage n
Retentate mass M_i =	$M_{i0}X^{(1-S_i)}$	$M_{i0}e^{-S_i(N+\ln X)}$	$[M_{i0}/S_i] \left[1 - (1 - S_i)e^{-S_i\tau(1-\frac{1}{X})} \right]$	
Area sizing A =	$\frac{(F-R)}{J}$	$\left(\frac{F}{J} \right) \left(\frac{1-1/X}{J_{conc}} + \frac{N/X}{J_{diaf}} \right)$	$\left(\frac{F}{J} \right) \left(\frac{1-1/X}{J_{conc}} \right)$	$P_n/J_n = F_n(1 + N_n - 1/X_n)/J_n$ per stage n
Comments	Simplest system and control scheme	Limited to X < 40 Smaller area or process time	Limited to X < 100 Minimize fed-batch ratio to minimize area	For multistage $F_n = R_{n-1}$

Where F feed volume (batch) or feed flow (continuous), R retentate, P permeate, D diafiltrate, V batch retentate volume, A membrane area, t process time, J flux (volumetric flow per unit area), J = average flux over step, C_i solute i concentration, M_i mass of solute i, S_i solute i observed passage through the membrane (C_{permeate}/C_{feed}), r fed-batch ratio (feed volume/ recycle tank volume = F/R), X volume reduction factor (F/R), N diavolumes (D/R for batch or D/F for continuous), n stage number n of multistage continuous system

involves partial recycle of the retentate. This configuration allows a higher crossflow and higher membrane fluxes compared to single pass for concentrated systems running in the polarized region of the flux curve. Compared to batch operation, setup and cleaning times between batches are significantly reduced so there is higher productivity on invested capital. As a result, continuous systems are common for large-scale processing. Continuous operation is frequently performed as a multistage operation where the retentate from one system becomes the feed for the next system. Each stage runs at a different concentration and the total area requirements are less than for a single stage. After about four stages, the system approaches batch operation as a minimum area. The residence time and number of pump passes is in-between single-pass and batch operation, depending on the fraction of retentate recycled.

Batch operation involves recycling the retentate to the feed tank to create a multipass flow of the feed through the module. The compositions in batch systems change over time. High flow rates generate better fluxes but recycling is necessary to generate either the desired permeate flow or a concentrated retentate. Multipass operation increases residence times and pump passes that may degrade retentate components. For systems requiring high pressures to generate permeate flow, it is useful to run the entire system at high pressure to save energy. As before, unsteady-state solvent and component mass balances can be written for batch operation and combined and integrated to yield concentration behavior. TFF systems have a maximum volume reduction capability, typically about 40x. This arises because tanks must be large enough to hold the batch volume while allowing operation at a minimum working volume. The minimum working volume may be limited by air entrainment into the feed pump, mixing in the feed tank, or level measurement capabilities.

Fed-batch operation extends the volume reduction capability to 100x and provides some flexibility in processing a variety of batch volumes in a single skid. For a fed-batch operation, the retentate is returned to a smaller recycle tank, not

the large feed tank. Feed is added to the recycle tank as permeate is withdrawn to maintain a constant recycle tank volume. The recycle tank can allow a smaller working volume without entrainment. Reducing the size of the recycle tank results in just a section of the pipe or bypass line that returns the retentate directly into the pump feed. Fluid from the feed tank is added slowly into this recirculation loop. This allows a holdup volume consisting of just the recirculation loop. This configuration can be problematic to flush, vent, and drain leading to cleaning and product recovery issues. Fed-batch retentate concentrations exceed the batch concentrations until the curves intersect and any further concentration would proceed in batch mode. The benefits sought from higher concentrations can lead to other problems such as reduced fluxes, larger area and pumps, possible denaturation, and extra lines that may have issues with cleaning and product recovery. This has not only caused significant commissioning and validation delays but also led to the scrapping of a process skid as unworkable. The number of pump passes will also be higher, leading to more potential solute degradation. Fed batch and bypass should be used only when necessary.

Diafiltration mode involves adding a new buffer to the system while withdrawing permeate at the same rate so the tank level remains constant. Over time, the retained solute sees a buffer change. This is characterized by the diavolumes N , the ratio of buffer volume added to tank volume for batch systems, and the ratio of buffer flow to feed flow for continuous systems. Table 1 shows how solute concentrations change with N . A fully retained solute ($S_i = 0$) maintains its retentate concentration constant at the initial value. For fully passing solutes, >4.5 diavolumes are needed to achieve a specification of $<1\%$ of the original buffer components. Incomplete mixing (due to dead legs and liquid droplets on tank walls) becomes significant at high diavolumes. It is common to add an extra 1–2 diavolumes as a safety factor to ensure complete buffer exchange. For final formulation pharmaceutical applications, 8–10 diavolumes are standard.

Diafiltration usually takes much more time than concentration. When a fully retained solute controls the flux by the gel model, the batch diafiltration time is given by

$$t = \left(\frac{V_a}{A}\right) \left(\frac{N/X}{k \ln \left(\frac{C_g}{C} \right)} \right), \text{ where } C \text{ and } X \text{ are related}$$

as in Table 1. This equation shows that more initial volume reduction and higher concentration lead to reduced batch volume and lower diafiltration fluxes. A minimum time solution exists when $C = C_g/e$.

UF Transport (Ultrafiltration Transport)

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UF membranes are porous solids that selectively retain large solutes and pass liquid solvent and small solutes. The interconnected porous network is sometimes described as a percolating foam structure. It is commonly described by a lognormal distribution of parallel cylindrical pores. Laminar flow of pure solvent through an incompressible membrane follows Darcy's law $J = L_m \cdot TMP$ where J is the flux or volumetric flow per unit membrane area, TMP is the transmembrane pressure difference across the membrane, and L_m is the constant membrane permeability. For parallel cylindrical pores of the same radius r , the permeability is $L_m = \frac{er^2}{8\mu l}$ where ε is the membrane porosity, μ is the fluid viscosity, and l is the membrane thickness. Any retained solute will accumulate on the upstream membrane surface causing an osmotic pressure Π . Membrane fouling reduces the membrane permeability to L_f . Process flow is described by the osmotic model $J = L_f(TMP - \sigma_0 \Delta \Pi)$ where σ_0 is the osmotic or Staverman reflection coefficient. For a totally retained solute, $\sigma_0 = 1$, and for a totally passing solute, $\sigma_0 = 0$. When $TMP < \Delta \Pi$, reverse flow is observed.

Retained solute will continue to accumulate for flow normal to the membrane surface J (normal flow filtration or NFF) but will reach a steady state when flow tangential to the surface v is added (tangential flow filtration or TFF). Most UF is run in TFF mode to maintain high fluxes for economical operation. For steady state where back diffusion balances entrained solute convected to the surface, the wall concentration $C_w = C_b \exp(J/k)$ for bulk concentration C_b , flux J , and mass transfer coefficient k . Retained solutes are reversibly held in a polarization or "gel" layer at the membrane surface at $\sim 1 \text{ g/m}^2$. The solute concentration at the membrane surface or "wall" operation at low concentrations (linear region) follows Darcy's law, but operation at high concentrations (polarized region) results in a flux that is independent of TMP but dependent on tangential flow v and solute bulk concentration C . This is empirically described by the gel flux model $J = kv^n \cdot \ln(C_g/C)$ where kv^n is the mass transfer coefficient and C_g is a constant "gel point" wall concentration. An actual gel is not formed. The osmotic model describes the flux across the linear and polarized regions. These models strictly apply to a uniform upstream, while in membrane modules, properties change along the upstream channel. The models can be integrated along the feed channel but are commonly used with an average TMP across the feed channel and feed velocities and concentrations.

A hydrodynamic analysis of steady-state solute flux by diffusion and convection along a pore yields a net solute flux of $N = [\phi K_c J / \varepsilon] [C_{wall} \exp(Pe_m) - C_{permeate}] / [\exp(Pe_m) - 1]$. The membrane Peclet number is $Pe_m = [Jl/D_\infty] [\phi K_c / \varepsilon \phi K_d]$ for solute-free solution binary diffusivity D_∞ , partitioning coefficient ϕ , convective hindrance coefficient K_c , and diffusive hindrance coefficient K_d . Pore shapes fall in-between cylindrical and slit geometries in terms of solute and pore wall interactions. For a spherical solute in a cylindrical pore, $C_{pore}/C_{wall} = \phi = (1 - \lambda)^2$ where $\lambda = r_{solute}/r_{pore}$, while asymptotic analysis yields $K_c \approx [2 - (1 - \lambda)^2] \exp(-0.7146\lambda^2)$ and $K_d \approx (1 - \lambda)^{-13/2}$. For a

spherical solute in a slit pore, steric considerations imply an equilibrium partitioning $C_{\text{pore}}/C_{\text{wall}} = \phi = (1 - \lambda)$ where $\lambda = r_{\text{solute}}/r_{\text{pore}}$, while asymptotic analysis yields $K_c \approx (3 - \phi)^2 [1/2 - \lambda^2/6]$ and $K_d \approx (1 - 1.004\lambda + 0.418\lambda^3 + 0.21\lambda^4 - 0.619\lambda^5)$. The “actual” solute sieving coefficient becomes $S_a = C_{\text{permeate}}/C_{\text{wall}} = S_\infty \exp(\text{Pe}_m) / [S_\infty + \exp(\text{Pe}_m) - 1]$ where $S_\infty = \phi K_c = 1 - \sigma_0$ is the asymptotic sieving coefficient for large Pe_m where convection dominates. The presence of surface charges reduces both membrane permeability and solute sieving coefficients. Average sieving across a membrane thickness from the wall to the permeate requires integration across the pore size distribution. Measured sieving coefficients from the bulk feed to the permeate requires accounting for polarization. Solutes are diluted within pores, but multicomponent interaction is required within the polarization layer where large solute polarization reduces the sieving of smaller solutes. Sieving along devices requires integration along the feed channel.

Ultrafiltration (UF)

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Ultrafiltration (UF or UF/DF) is a unit operation that separates large solutes from small solutes and solvents. Larger pore membranes are referred to as microfiltration (MF), while smaller pore filters are referred to as reverse osmosis (RO). There is some nomenclature confusion as membrane scientists refer to a loose RO charged membrane as a nanofilter, while bioprocessors refer to a loose UF membrane as a nanofilter that removes nanometer-sized viruses.

UF employs thin porous solid UF membranes as either flat sheets or tubes (see chapter “► [UF Membranes \(Ultrafiltration Membranes\)](#)”). These perform separations by retaining and passing solutes primarily based on their size and secondarily based on solute-surface interaction by charge or

other fields (see chapter “► [UF Transport \(Ultrafiltration Transport\)](#)”). Pressures of 0.2–1.0 MPa drive liquid solvents (primarily water) through the membrane. Since retained solid buildup can cause the solute flow to rapidly decline, most UF systems are run in tangential flow filtration (TFF) mode with a significant velocity tangent to the membrane surface. This enhances back transport away from the surface and leads to steady-state operation at reasonably economical solvent fluxes (volumetric flow per unit area).

UF membranes are fabricated into modules that allow for convenient assembly and operation in modular systems. Commercial module formats include hollow fiber bundles, tubular assemblies, spiral wound assemblies, and cassettes. Stirred cell devices are commonly used for research since they require little volume, operate at uniform conditions across their surface, and are well characterized.

Typical UF process operating steps include: assembly, water flush, integrity testing, buffer flush, processing, recovery flush, cleaning, sanitization, disassembly, and storage. Assembly of modules into a holder is required for a new operation or when the filters have reached expiration and need to be replaced. Water flushing thoroughly wets the membrane and removes extractables and antimicrobial or humectant storage agents. Integrity testing involves measuring downstream airflow with pressurized air upstream. Defects or installation leaks will show up as high air flows. Buffer flush conditions the membrane to limit product denaturation and membrane fouling. Processing may follow concentration or diafiltration in continuous or batch operating modes (see chapter “► [UF Membranes \(Ultrafiltration Membranes\)](#)”). Diafiltration involves adding a new buffer that displaces the old buffer leaving in the permeate while retaining the desired solute. Recovering high value product from batch systems involves a low pressure air blowdown or reverse buffer flush through the modules. System cleaning involves thoroughly flushing out remaining product and recirculating a cleaning solution at the desired time, temperature, and concentration. Multiple fouling agents

may require cleaning steps with multiple cleaning agents (e.g., NaOH for proteins, acid for precipitated salts). Cleaning effectiveness is measured by the restoration of water permeability. Sanitization involves recirculating a sanitizing solution at the desired time, temperature, and concentration. This is frequently done as a separate additional step even if the chemical is the same as for cleaning. The rationale is to ensure that no protective biofilm is present that would prevent sanitization from being effective. At the end of a production campaign, modules can be stored in a liquid storage solution. Modules at the end of their life are discarded. Lifetimes can be set by number of uses, age, or process performance such as permeability, retention, integrity, and feed channel pressure drop.

Key UF membrane properties include retention capability, solvent permeability, chemical compatibility, mechanical strength for module fabrication and repeated use, consistency, and cost. UF membranes come with a nominal molecular weight limit (NMWL) rating of 1.0–5,000.0 KDa. The smaller rating means a tighter filter able to retain a smaller solute with a lower molecular weight. While these ratings are convenient for testing and rough selection, solute retention is based on effective solute dimensions and not on molecular weight. Nonspherical solutes will orient themselves under shear so that their major axis is parallel to the pores. Linear chain dextrans and DNA show a higher passage than globular proteins of the same molecular weight. The effective solute radius can increase more than four times as a result of surface charge. Ratings are not standardized among vendors and depend on the marker solute selected (e.g., protein, dextran in a particular buffer) and the level of retention selected for the marker solute (e.g., 90 %). Retention is also affected by fouling due to adsorbed components and polarized solutes on the membrane surface. A rule of thumb for selecting membrane NMWL is to take 0.2–0.3 of the MW of the solute that is to be retained by the membrane. This should be taken as a rough guide to select membranes for testing.

Selected membrane module manufacturers in 2012 include: EMD Millipore (Billerica, MA, USA), Pall (Port Washington, NY, USA),

Sartorius (Germany), Asahi Kasei (Japan), GE Energy (Raytown, MO, USA), Siemens (Warrendale, PA, USA), TriSep (Goleta, CA, USA), Aquatech (Canonsburg, PA, USA), Degremont Technologies (Richmond, VA, USA), Spintek (Los Alamitos, CA, USA), Koch Membrane Systems (Wilmington, MA, USA), Berghof (Mühlhausen, Germany), Daicel (Tokyo, Japan), DSS (Silkeborg, Denmark), Matrix (Oceanside, CA, USA), and Nitto Denko Hydranautics (Oceanside, CA, USA).

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Ultrafiltration Applications

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UF membranes perform separations based on solute size. They have retention ratings of 1–5,000 K for roughly spherical solutes and can retain solutes of 10–1,000 Å or larger in diameter (roughly 300–1,000 KDa) such as colloids, large molecules, and nanoparticles. Smaller solutes and solvents pass through the ultrafilter. UF membranes retain smaller solutes than microfiltration membranes and larger solutes than reverse osmosis membranes.

Most commercial operations are run as tangential flow filtration (TFF), but dilute solutions such as water treatment or small-scale sample preparation are run as normal flow filtration (NFF). Virus-retaining filters, sometimes referred to as nanofilters, are on the most open end of UF and

Ultrafiltration Applications, Table 1 Ultrafiltration applications

Application	Paint recovery	Whey processing	Biopharmaceutical purification	Water treatment	Juice processing
Membrane	PES	PES	Cellulose, PES, PVDF	PES	PES, PVDF
Module	Fibers	Spirals	Cassette	Fibers	Tubes
System	Continuous	Continuous	Batch, NFF	Continuous	Batch
Performance drivers	Cost, plugging	Cost	Recovery	Cost	Plugging, cost

can be run as NFF or TFF. The first large commercial application of UF was paint recycling, followed by dairy whey recovery in the mid-1970s. Applications can be described as clarification of a permeate product (e.g., water purification), concentration of a retentate product (e.g., paint, dairy, and pharmaceuticals), or solute purification (e.g., virus/protein separation and buffer exchange). UF applications are enabled by low temperature and low-cost operation, particularly with membrane reuse. UF processes can vary significantly between applications due to differing requirements and relative costs.

Automobiles used to rust due to paint nonuniformity. Electrodeposition of cationic paint resin on automobiles (connected to the cathode) was developed to provide a uniform, defect-free coating with high corrosion resistance. This process deposits about 50 % excess paint on the surface that must be washed off. UF is used to retain and recover the washed paint to maintain a high paint concentration in the paint bath. The paint-free permeate is used for washing. Paint recovery to reduce losses and lower system costs makes the process economical.

During cheese making, the coagulated milk or curd is used to make cheese, while the supernatant whey is a waste product rich in salts, proteins, and lactose. UF retains whey proteins while passing water, sugars, and salts. The retentate proteins are used as soft cheese products and animal feed supplements. The MMV process concentrates the milk by UF after centrifugation removes the cream and before coagulation to improve yields and reduce disposal costs.

UF is used in biopharmaceutical purification to retain proteins, viruses, bacterial vaccines, and nucleic acids. Water and buffers pass through the membrane. Initial UF concentration of clarified

fluids or lysates reduces process volumes to decrease subsequent column sizes and increase binding. Diafiltration UF changes buffer conditions (for loading on to columns) and to concentrate and change buffers (for final formulation into a storage buffer). For drug products with potential viral contaminants (sourced from mammalian cells or human and animal blood plasma), virus removal filters employed in either a TFF or NFF mode retain the viruses, while the drug product is recovered in the permeate. UF has displaced size exclusion chromatography (SEC) for buffer exchange due to its lower cost and ability to run higher protein concentrations. These applications require high yields, maintaining high purity, consistent operation, and scale-up of the valuable product.

UF is used to clarify various fruit juices (apple, grape, pear, pineapple, cranberry, orange, and lemon) which are recovered as the permeate. UF has also been used to remove pigments and reduce browning in wine production. Low-cost operation is required.

Wastewater treatment and water purification applications employ UF in a TFF or NFF mode to produce permeate product with reduced colloids, pyrogens, and viruses. Oil droplets in wastewater are retained by UF for recycle or disposal at significantly reduced volumes (Table 1).

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Ultrafiltration Membrane Bioreactor

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Synonyms

Membrane bioreactor using ultrafiltration membranes

Introduction

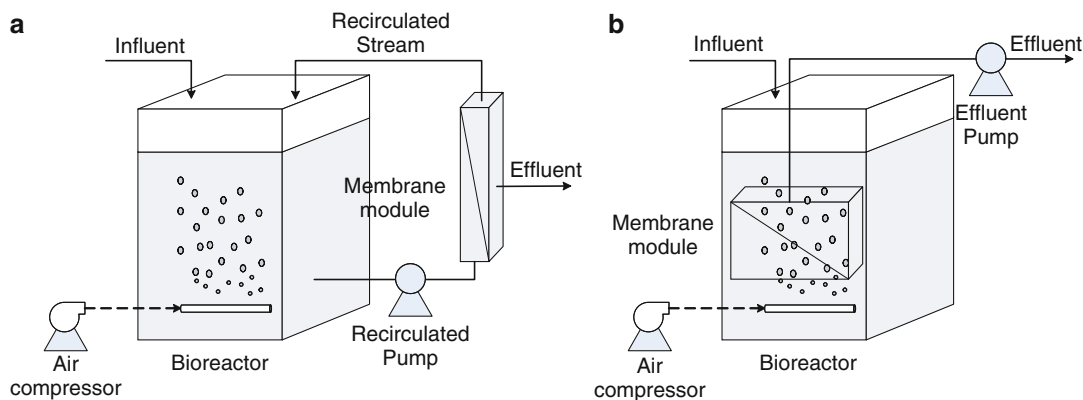
Membrane bioreactor (MBR) is the combination of a membrane process with an activated sludge bioreactor and is now widely used for municipal/domestic and industrial wastewater treatment. Pressure-driven membrane separation is usually applied in MBR processes even though other novel membrane separation systems (e.g., forward osmosis membrane) have been developed. Typical pressure-driven filtration types that could be used in MBRs include dynamic membrane filtration, microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) (Wang et al. 2008; Meng et al. 2009), while MF and UF membranes are commonly used (Wang et al. 2008). MBRs using UF membrane can be termed as ultrafiltration MBRs.

In UF processes, suspended solids and solutes of large molecular weight present in feed solutions (e.g., water and wastewater) are retained while water and low molecular weight solutes pass through the membrane and flow into the permeate. The membrane pore size of UF is generally in the range of $0.002 \sim 0.1 \mu\text{m}$, and the corresponding molecular weight cut-off (MWCO) roughly ranges from 1 to 500 kDa. The transmembrane pressure (TMP) of UF is about $0.1 \sim 0.7 \text{ MPa}$. Commercial UF membranes are usually asymmetric with a thin skin layer ($0.1 \sim 1.0 \mu\text{m}$ thick) and a highly porous layer ($50 \sim 250 \mu\text{m}$ thick) (Xiarchos et al. 2003), although some symmetric membranes are also available. The porous skin

layer of UF membranes is usually exposed to the feed solutions. Typical UF membrane materials include polyvinylidene fluoride, polyether-sulphone, polyacrylonitrile, polyimide, polytetrafluoroethylene, polypropylene, polysulfone, cellulose acetate, aliphatic polyamides, and ceramics (e.g., zirconium and aluminum oxides) (Xiarchos et al. 2003; Wang et al. 2008). Due to the introduction of membrane separation, MBRs have several prominent advantages including improved effluent quality, higher volumetric organic load, reduced footprint, and less sludge production compared to conventional activated sludge (CAS) processes, and thus have attracted much attention in the past two decades.

In UF MBR processes, MBR systems are generally comprised of two configurations: submerged (immersed or integrated) MBRs and side-stream (recirculated or external) MBRs (see Fig. 1) based on whether the membrane modules are immersed in the main reactor or not. In general, submerged MBRs consume much less energy than side-stream MBRs due to the absence of a high-flow recirculation pump. Compared with side-stream MBR, submerged MBR is more popular in water and wastewater treatment because of its lower operational cost (Wang et al. 2008). Side-stream MBRs are widely used for industrial wastewater treatment.

Membrane fouling is inevitable for MBRs, resulting from the interactions between the membrane material and the components of activated sludge (biomass). The potential foulants include suspended solids, colloids, biopolymers (e.g., soluble microbial products and extracellular polymeric substances), and so on, while biopolymers are currently regarded as major contributors to membrane fouling (Meng et al. 2009; Wang et al. 2013). Membrane filtration performance can be enhanced through modifying membrane materials, optimizing operating conditions, and bettering sludge characteristics. Membrane cleaning is periodically performed for maintaining the sustainable operation of MBRs during long-term operation. The well-designed cleaning protocols are comprised of backwashing, chemically enhanced backwashing, maintenance cleaning, and recovery cleaning. The prevalent



Ultrafiltration Membrane Bioreactor, Fig. 1 MBR configuration: (a) side-stream membrane bioreactor; (b) submerged membrane bioreactor

cleaning agents include NaOCl (sodium hypochlorite) and citric acid targeting organic fouling and inorganic fouling, respectively. In general, cleaning-in-place is preferred while offline cleaning is needed in MBRs if the filtration performance cannot be sustained by using online cleaning.

Cross-References

- [Aerobic Membrane Bioreactor](#)
- [Membrane Bioreactors for Treatment of Tannery Effluents](#)
- [Membrane Biotechnology](#)

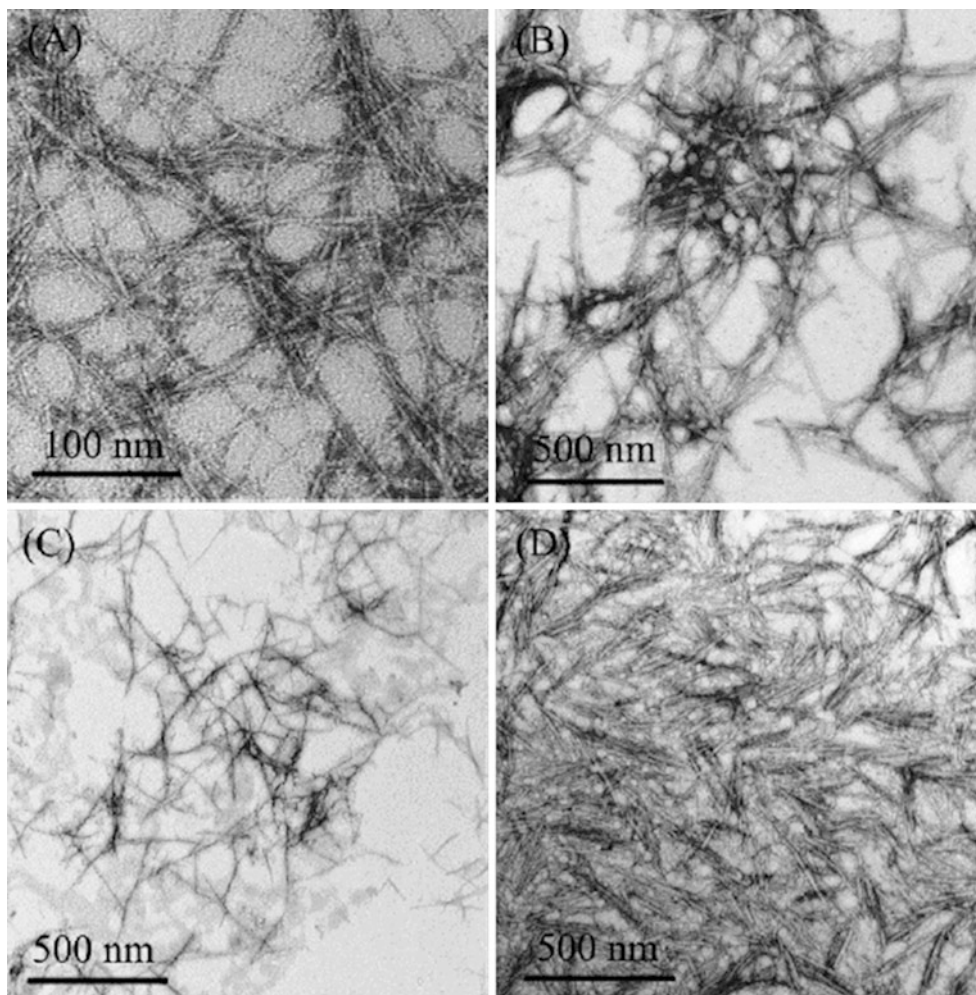
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Ultrafine Nanofibers

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Ultrafine nanofibers are nanofibers with typical fiber diameters ranging from 1 to about 10 nm. They can be fabricated by using a variety of techniques, such as self-assembly, electrospinning, or chemical catalysis. A novel technology has been developed to fabricate ultrafine polysaccharide nanofibers (e.g., ultrafine cellulose nanofibers) by using a combination of chemical and mechanical treatments on natural resources, such as wood, cotton, and crab/shrimp shell (chitin) (Ma et al. 2011). The fiber diameter of the achieved ultrafine nanofibers was 5–15 nm with various fiber lengths of a few hundred nanometers to a few microns. The chemical treatment, typically, is a selective oxidation of C6-hydroxyl groups in cellulose with the TEMPO/NaBr/NaClO aqueous system. After oxidation, a mechanical treatment, such as grind, sonication, or/and homogenization, is applied to defibrillate the fiber bundles. Therefore, ultrafine cellulose nanofibers with nominal fiber diameters of 5–15 nm in aqueous suspension can readily be obtained.



Ultrafine Nanofibers, Fig. 1 Ultrafine nanofibers from different natural polysaccharide sources (Ma et al. 2012b)

The fabricated ultrafine cellulose nanofibers offer many unique advantages, including (1) high surface-to-volume ratio ($\sim 600 \text{ m}^2/\text{g}$); (2) high chemical resistance and strong mechanical properties; (3) super-hydrophilic surface property; (4) surface functionalized with carboxylate groups, hydroxyl groups, and/or aldehyde groups; (5) water dispersible and stable suspensions; (6) and benign environmental properties. Based on these advantages, one of the novel applications of ultrafine cellulose nanofibers is that cross-linked ultrafine fibers can be used as a barrier layer in a highly permeable nanocomposite membrane for water purification. The super-hydrophilic surface of the ultrafine cellulose

nanofibers is also of benefit to the antifouling property of the membrane. Most importantly, directed water channels can be formed between the surface of ultrafine (cellulose) nanofibers and the surface of the barrier polymer matrix, thereby significantly increasing the permeability of the membrane without losing the rejection ratio (Ma et al. 2012a, b) (Fig. 1).

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Ultrahigh Molecular Weight Polyethylene

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Ultrahigh molecular weight polyethylene (UHMWPE), also known as high-modulus polyethylene (HMPE), is a subset of the thermoplastic polyethylene. Polyethylene is a polymer formed from ethylene (C_2H_4), which is a gas having a molecular weight of 28 g/mol. The generic chemical formula for polyethylene is $-(C_2H_4)_n-$, where n is the degree of polymerization. A schematic of the chemical structures for ethylene and polyethylene is shown in Fig. 1.

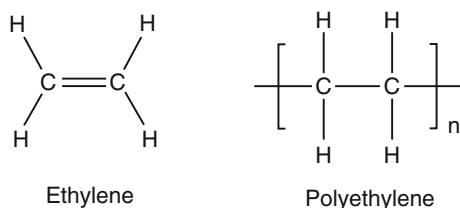
There are several kinds of polyethylene (LDPE, LLDPE, HDPE, UHMWPE), depending upon the degree of polymerization or molecular weights and chain architectures. LDPE and LLDPE refer to low-density polyethylene and linear low-density polyethylene, respectively. These polyethylenes generally have branched and linear chain architectures, respectively, each with a molecular weight of typically less than 50,000 g/mol. High-density polyethylene

(HDPE) is a linear polymer with a molecular weight of up to 200,000 g/mol (Steven 2009).

For an ultrahigh molecular weight polyethylene, the molecular chain can consist of as many as 200,000 ethylene repeat units. Thus, molecular weight ranges in the millions, usually between two and six million. The longer chain serves to transfer load more effectively to the polymer backbone by strengthening intermolecular interactions. This results in a very tough material, with the highest impact strength of any thermoplastic presently made (Stein 1999). UHMWPE is a unique polymer with outstanding physical, chemical, and mechanical properties. Most notable are its chemical inertness, lubricity, impact resistance, and abrasion resistance. Table 1 summarizes the physical and mechanical properties of UHMWPE.

Owing to its excellent properties, UHMWPE is widely used as a biomaterial such as in orthopedics as a bearing material in artificial joints. One of the major limiting factors of UHMWPE implant is its wear and damage with time, thus having only a finite lifetime. Cross-linking of the UHMWPE chains is found to be the promising method to dramatic reductions in wear, improving the performance in biomedical applications (Steven 2004).

Recently, research has been conducted for the modification of the UHMWPE surface by grafting with different techniques such as radiation, chemical, and plasma grafting. Since UHMWPE



Ultrahigh Molecular Weight Polyethylene, Fig. 1 Schematic of the chemical structure of ethylene and polyethylene

Ultrahigh Molecular Weight Polyethylene, Table 1 Typical average physical properties of ultrahigh molecular weight polyethylene (UHMWPE) (Li and Burstein 1994)

Property	UHMWPE
Molecular weight (10^6 g/mol)	3.5–7.5
Melting temperature ($^{\circ}\text{C}$)	132–138
Poisson's ratio	0.46
Specific gravity	0.925–0.945
Tensile modulus of elasticity ^a (GPa)	0.5–0.8
Tensile yield strength ^a (MPa)	21–28
Tensile ultimate strength ^a (MPa)	39–48
Tensile ultimate elongation ^a (%)	350–525
Impact strength, Izod (J/m of notch; 3.175 mm thick specimen)	>1070 (no break)
Degree of crystallinity (%)	39–75

^aTesting conducted at 23 $^{\circ}\text{C}$

is a semicrystalline polymer, its crystalline part normally remained unchanged, while the amorphous part can be grafted. The UHMWPE membrane has been evaluated as a proton exchange membrane for fuel cells (Sherazi et al. 2009, 2010).

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Urease Immobilization on Membranes

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Enzyme immobilization within membrane pores or onto membrane surface has gained growing interest due to controllable transport of reaction substrates and products through the membrane. This is particularly important when the product acts as an inhibitor. Also, high surface area of the membranes offers a potentially higher enzyme loading. Urease is an enzyme most extensively studied for immobilization and catalyzes the

hydrolysis of urea to ammonium and carbon dioxide. Nonenzymatic urea hydrolysis requires high temperatures and pressures and biological conversion of urea nitrogen to dinitrogen suffers from instabilities of microbial bed. The method based on the hydrolysis of urea by urease immobilized on a suitable support material is an attractive and an alternative removal method.

The choice of a support material for enzyme immobilization is important to minimize the loss of enzyme activity. The membrane material should have high affinity to proteins, available reactive functional groups for direct enzyme attachment or for chemical modification, mechanical stability, and regenerability. The membranes from natural polymers may have restricted applications since the abundance in hydrogen bonding among the polymer chains may result in a decrease in flexibility, the excellent affinity to proteins may make them easily eroded by bacteria, and high hydrophilicity may cause the membranes to swell in a wet atmosphere. Due to these drawbacks, synthetic membranes were preferred as enzyme carriers because of their low cost, easy surface modification, resistance to biodegradation, and thermal and chemical stabilities.

Urease was immobilized onto various supports and a detailed review of these studies has been published by Krajewska (2009). The membranes used as a support material were made from nylon, silk cloth, polypropylene fabric, poly(hydroxyethyl methacrylate-*co*-glycidyl methacrylate), polyacrylonitrile, methoxypolyethylene glycol 5000, poly(*N*-isopropylacrylamide-*co*-*N*-acrylosuccinimide-*co*-2-hydroxyethyl methacrylate), poly(2-hydroxyethylmethacrylate), chitosan-poly(glycidylmethacrylate) copolymer, ethylene-vinyl alcohol, nylon 6/6, acrylamide-grafted poly(ethylene terephthalate) fibers, tris(hydroxymethyl)phosphine polyetheramine copolymer, chitosan, collagen-glycidyl methacrylate graft polymer, cyanuric chloride DEAE-cellulose ether, poly(acrylonitrile)-chitosan composite, expanded PTFE, polyethylene, polyamide, polyaniline, poly(ethylene terephthalate) fibers, and aminated polysulfone. In these studies, urease was immobilized by covalent attachment where reactive functional groups on the surface of the

membrane were generated by different surface modification techniques and by cross-linking with multifunctional, low molecular reagents. In recent years, the layer-by-layer assembly technique was shown to be an efficient method for enzyme immobilization (Smuleac et al. 2006). The method involves layer-by-layer deposition of oppositely charged polyelectrolytes by consecutive, alternating immersion of a charged substrate into aqueous solutions of an anionic and a cationic polyelectrolyte. Since enzymes are multiply charged molecules, the layer-by-layer (LBL) assembly offers a simple method to perform the immobilization. In some cases, electrostatic interactions in the assembly help stabilize the enzymes to maintain their activity. The LBL method was used to immobilize urease on polystyrene particles, silicon microchannels, or NH_3 electrode (Krajewska 2009). Guedidi et al. (2010) immobilized urease on polyacrylonitrile-based membranes using LBL assembly. The optimum pH for both native and immobilized urease was found to be at about seven. Immobilized form of urease retained higher activity at lower pH than the soluble counterpart. Immobilization onto a polyelectrolyte layer (urease forms the last layer of the assembly) resulted in a higher catalytic activity than that of enzyme directly immobilized on the membrane which clearly indicates the beneficial effect of a polyelectrolyte environment. Immobilization of urease in between two polyelectrolyte layers decreased the activity compared to the previous case most probable due to the diffusion-limited accessibility of the catalytic site. Adsorption of negatively charged urease directly onto negatively charged support resulted in a loss of enzyme activity in a short period of time. On the other hand, immobilization of urease between two polyelectrolyte layers appeared to bring better environment to ensure long-term enzyme stability.

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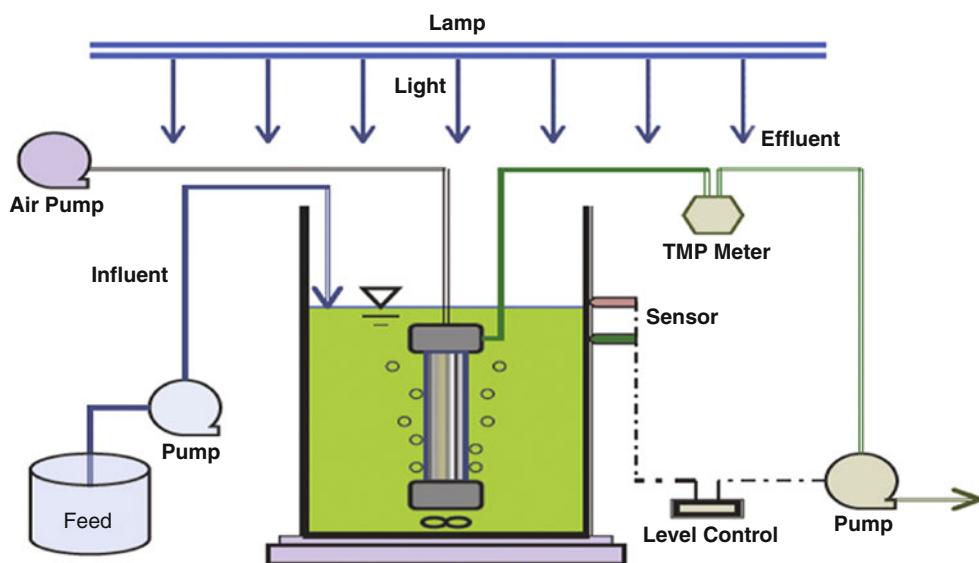
Use of Microalgae in MBR

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Membrane photobioreactor is a system that integrates microalga growth with membrane separations for nutrient (N and P) removal from wastewater and algal biomass production for biofuels, as shown in Fig. 1.

Commercial use of algal cultures for wastewater treatment and mass production of algal biomass has a history over one century. Biological wastewater treatment with microalgae is particularly attractive due to their photosynthetic capabilities in converting solar energy and CO_2 into useful biomass and uptaking nutrients (nitrogen and phosphorus) into microalgae biomass (Rawat et al. 2011). The use of membrane bioreactors for microalgae wastewater treatment simplifies the operation of microalgae harvesting and produces effluent with superior quality. Membrane bioreactor (MBR) has been widely used for municipal and industrial wastewater treatment, due to the advantages of small footprint, high productivity, and superior quality of effluent for water reuse and system closure. However, nutrient (N and P) removal has been a challenge for both aerobic MBR and anaerobic MBR. The capability of microalgae for nutrient uptake and CO_2 as carbon source for growth makes it an ideal candidate for sustainable wastewater treatment. The integrated MBR-microalgae processes have received much attention in recent years as a next-generation



Use of Microalgae in MBR, Fig. 1 Schematic diagram of a membrane photobioreactor (Adapted from Xu et al. (2014))

technology for sustainable wastewater treatment. There are three types of microalgae membrane bioreactor processes: (1) an integration of conventional activated sludge process with membrane photobioreactor, (2) an integration of MBRs (aerobic MBR or anaerobic MBR) with conventional microalgae photobioreactor, and (3) an integration of MBRs (aerobic MBR or anaerobic MBRs) with a membrane photobioreactor. For the second scenarios, a microalgae photobioreactor was used to treat the effluent of an anaerobic MBR for municipal wastewater treatment (Ruiz-Martinez et al. 2012). At a solid retention time of 2 days, the microalgae photobioreactor achieved a mean biomass productivity of 234 mg/d and a nutrient removal efficiency of 67.2 % for ammonium (NH_4^+-N) and 97.8 % for phosphate (PO_4^{3-}P) (Ruiz-Martinez et al. 2012). In the third scenarios, an aerobic MBR-membrane photobioreactor system was tested for domestic wastewater treatment (Singh and Thomas 2012). Similarly, a comparative study between the second and third scenarios found that the use of membrane photobioreactor significantly increased the microalgae biomass concentration and volumetric productivity by 3.5 and 2 times, respectively, in addition to the

elimination of microalgae washout and superior effluent quality (Marbelia et al. 2014). The membrane photobioreactor was able to remove an average 50 % of NH_4 , 75 % of NO_2 , 35 % of NO_3 , and 60 % of PO_4 consistently from the MBR effluent under the conditions tested (Marbelia et al. 2014). Integrated MBR-microalgae processes represent a next generation of technology for sustainable wastewater treatment.

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Use of Streaming Potential Measurements for Characterization of Both Membrane/Electrolyte Interface and Protein Fouling Effect

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Electrical nature of external and internal (pore-wall) membrane surfaces is significant for salt rejection and transport characterization of RO and NF membranes or for filtration of solutions containing macromolecules and colloids. Electrokinetic measurements are usually performed for characterization of membrane/electrolyte interfaces and to estimate changes associated to membrane fouling as a result of cake layer formation (external fouling) or pore narrowing/plugging (internal fouling).

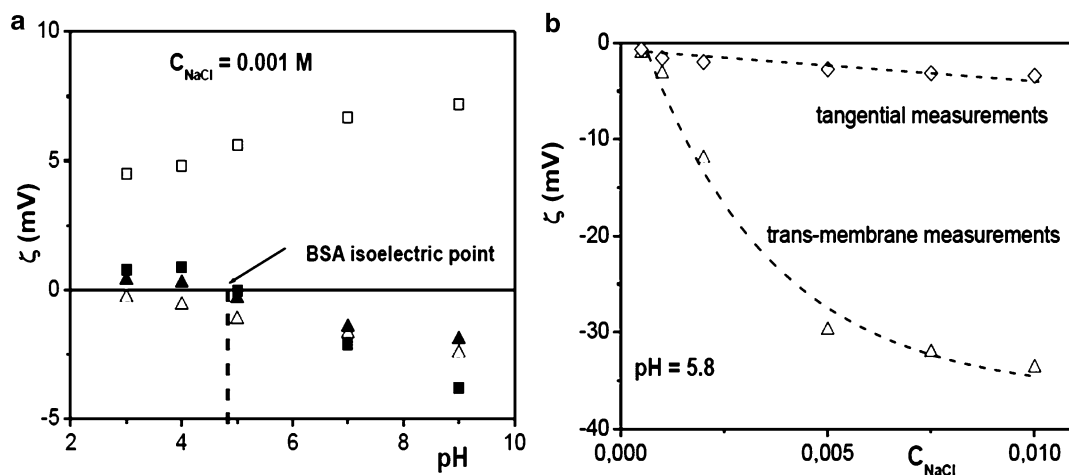
Zeta potential (ζ) is the stationary electrical potential at the shear plane between fixed and mobile ions in the double layer associated to solid-liquid charged interfaces. For weakly charged walls or wide channels/pores, ζ -potential is obtained from streaming potential coefficient $(\Delta\phi_{st}/\Delta P)_{I=0}$ by Helmholtz-Smoluchowski equation (Hunter 1988):

$$\zeta_{H-S} = (\lambda_e \eta \epsilon_o \epsilon) (\Delta\phi_{st}/\Delta P)_{I=0} \quad (1)$$

where λ_e , η , ϵ , and ϵ_o are the solution conductivity, viscosity, membrane dielectric constant, and vacuum permeability, respectively.

To show the potentiality of electrokinetic characterization, ζ -potential results for clean and BSA-fouled porous membranes, polymeric (GR, polysulfone $\langle rp \rangle \sim 0.1 \mu m$) and ceramic (Z100S, ZrO_2/Al_2O_3 on stain steel support $\langle rp \rangle \sim 0.06 \mu m$), by transmembrane measurements at different pHs (Lara and Benavente 2009), and tangential measurements changing NaCl concentration for a dense regenerated cellulose (RC) membrane are presented (Cañas et al. 2001).

Figure 1a shows the comparison of ζ values as a function of solution pH for GR and Z100S membranes. Polysulfone GR membrane exhibits electronegative character, but it is electropositive



Use of Streaming Potential Measurements for Characterization of Both Membrane/Electrolyte Interface and Protein Fouling Effect, Fig. 1 ζ -potential as a function of (a) pH for clean (Δ) and BSA-fouled (▲) GM

membranes, clean (□) and BSA-fouled (■) Z100S membranes; (b) concentration for clean GM (Δ) and RC (◇) membranes

for ceramic Z100S; moreover, ζ -potentials for GR membrane slightly vary due to BSA fouling, but they significantly change for the ceramic sample (from positive to negative), and practically the same isoelectric point ($\zeta = 0$) was obtained with both fouled membranes, which corresponds to the BSA isoelectric point. These results indicate the BSA coverage of pore walls for both fouled samples.

Figure 1b shows ζ -potential dependence on solution concentration for clean GR (through pores) and dense RC (along surface) membranes, indicating absorption of Cl-ions on internal (GR) or external (RC) membrane surfaces.

Analysis of electrokinetic surface charge density or charge density at shear plane ($\sigma_e = (2RT\varepsilon_0\varepsilon \kappa/F)\sinh(F\zeta/2RT)$) with the molar fraction of ions ($c \approx C_n/M_{H_2O}$) can give information on adsorption parameters using adequate models (homogeneous Langmuir model or heterogeneous Freundlich model (Benavente et al. 1993), and the following values for the chemical part of free adsorption energy (ΔG_{ch}) and total number of adsorption sites per membrane area (N) were obtained for GR and RC membranes assuming a Langmuir model:

$$\text{Polysulfone GR: } \Delta G_{ch} = -(18.9 \pm 0.7) \text{ kJ/mol, } N = (4.9 \pm 0.4) \times 10^{15} \text{ m}^{-2}.$$

$$\text{Cellulosic RC: } \Delta G_{ch} = -(25.7 \pm 0.7) \text{ kJ/mol, } N = (1.4 \pm 0.5) \times 10^{16} \text{ m}^{-2}.$$

Differences associated to membrane material can be obtained; the negative sign and low values of ΔG_{ch} indicate spontaneous adsorption of Cl-ions on membrane pore-wall or external surface.

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UV Irradiation

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UV radiation energy waves are the range of electromagnetic waves 100–400 nm long (between the X-ray and visible light spectrums), corresponding to photon energies from 3 to 124 eV. It is so named because the spectrum consists of electromagnetic waves with frequencies higher than those that humans identify as the color violet. The division of UV radiation may be classified as Vacuum UV (100–200 nm), UV-C (200–280 nm), UV-B (280–315 nm), and UV-A (315–400 nm). UV irradiation occupies only about 3–5 % of the total solar irradiance at the Earth's surface.

UV irradiation has many technical applications through the use of particular wavelength, including security, forensics, spectrophotometry, photolithography, sterilization, disinfecting drinking water, removing persistent organic compounds via photocatalyst, and initiating chemical reactions and others.

UV irradiation linked to membrane science and technology is manifested in three aspects.

1. UV irradiation for preparation, modification, and stimulation of polymeric membranes. For de novo preparation of membranes from low molar mass or soluble precursors, photo-initiated polymerization and photo

cross-linking are the main pathways, while photodegradation for pore formation is only rarely applied (He et al. 2009). For membrane modification, “grafting-from” and “grafting-to” are two commonly used strategies. The “grafting-from” method utilizes active species existing on a membrane surface to initiate the polymerization of monomers from the surface. For “grafting-to” method, polymer chains carrying reactive anchor groups at the end or on the side chains are covalently coupled to the membrane surface. Photostimulation of barrier properties is an attractive concept to create stimuli-responsive membranes and various ways to use photochromic moieties. Photoirradiation-based methods can be very versatile enabling technologies to improve the performance of polymeric membranes in technical separations (e.g., in gas separation, pervaporation, ultrafiltration, and microfiltration or as membrane adsorbers) and other processes (e.g., for controlled release or in sensor systems), and they will contribute to the development of entirely novel membrane-based materials (He et al. 2009).

2. The combination of photocatalysis utilizing UV irradiation with membrane separation, which is often called photocatalytic membrane reactors (PMRs). PMRs can be generally classified into two main configurations: (a) reactors with photocatalyst particles suspended in feed solution and (b) reactors with photocatalyst immobilized on/in the membrane. The major disadvantage of the configuration with photocatalyst in suspension is deterioration of the permeate flux and membrane fouling. PMRs with photocatalyst on/in membrane are

one solution for this problem. In this configuration, oxidation by hydroxyl radicals occurs on the external surface and within the pores of the membrane, while reactants are permeating in a one-pass flow. However, fixation of the photocatalyst often results in a loss of photoactivity and might cause destruction to the membrane structure (Mozia 2010).

3. UV irradiation for membrane fouling/biofouling control and membrane clean. UV irradiation integrated in membrane system is able to mitigate membrane biofouling, which is caused by deposition or growth of microorganisms on membrane causes. For the membrane with photocatalyst (such as TiO_2) on the surface or entrapped in, the fouling can be effectively controlled because the pollutants can be effectively degraded by the photocatalyst with UV irradiation during filtration process. The fouled membranes after membrane filtration can also be cleaned with only UV irradiation, which provides the photocatalyst-doped membrane self-cleaning property (Song 2012).

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Vacuum Membrane Distillation (VMD)

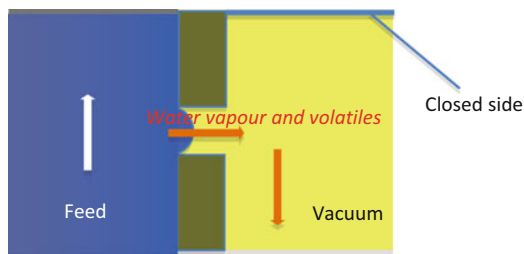
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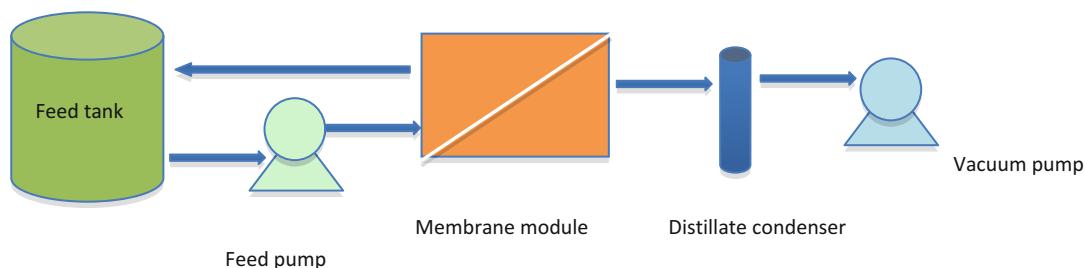
Vacuum membrane distillation (VMD) is one of the possible configurations of membrane distillation, where vacuum is applied at the distillate side in order to create the driving force for the water vapor and volatile transfer from the feed to the permeate side (Fig. 1).

The vacuum is achieved by means of a vacuum pump, and the distillate is recovered outside the membrane module in a refrigerated trap, where it condenses (at lab scale, liquid nitrogen is often used as condensing medium); see Fig. 2. As for the other membrane distillation configurations, membrane properties like pore size, porosity, and thickness affect the transmembrane flux, together with the temperature profile in the boundary layer of the liquid stream that makes the temperature at

the membrane surface (where the evaporation takes place) lower than that of the bulk. Nevertheless, it has to be pointed out that, in this case, the polarization phenomena occur only at the feed side, being the distillate one completely under vacuum. Moreover, the heat loss by conduction through the solid part of the membrane is negligible. For these reasons, the VMD is usually characterized by higher fluxes and energy efficiency than the other configurations. The high pressure difference established across the membrane could, however, increase the risk of membrane wetting.



Vacuum Membrane Distillation (VMD),
Fig. 1 Scheme of the vacuum membrane distillation



Vacuum Membrane Distillation (VMD), Fig. 2 A typical setup used for carrying out vacuum membrane distillation tests

Vacuum Membrane Distillation (VMD), Applications of

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Vacuum membrane distillation (VMD) can be applied to the treatment of aqueous streams for recovering purified water or for extracting specific volatile compounds. Concerning the first type of application, many studies have demonstrated the efficiency of the technique for liquid streams contaminated by nonvolatile species such as heavy metals or dyes discharged by textile companies (Criscuoli et al. 2008): in all cases, the distillate produced consists of purified water (able to be reutilized inside the productive plant or to be used for drinking/agriculture purposes) with rejection values generally higher than 99 %. Other positive performances are those related to the treatment of olive mill wastewaters (Garcia-Castello et al. 2010) and the recovery of fully demineralized water starting from brackish waters, seawaters, and reverse osmosis brines (Li and Sirkar 2005; Safavi and Mohammadi 2009; Méricq et al. 2011). In particular, for the application to salty solutions, two main benefits are claimed: the recovery of purified water and the production of a highly concentrated brine, with a consequent reduction of its volume and, therefore, of costs associated to its disposal. VMD can be

Vacuum Membrane Distillation (VMD), Applications of, Table 1 Main applications of VMD

Recovery of purified water from aqueous streams containing nonvolatile pollutants like heavy metals, dyes, etc.
Recovery of fully demineralized water from salty solutions and concentration of reverse osmosis brine
Concentration of fruit and vegetable juices
Recovery of volatile compounds like ethanol, ammonia, VOCs, etc., from aqueous solutions

also used for the concentration of fruit/vegetable juices (Al-Asheh et al. 2006; Zhao et al. 2008), again, with the aim of recovering water as distillate while producing a high concentrated retentate that can be easily stored and shipped.

Referring to the application of VMD to the extraction of specific volatile compounds contained in water streams, some examples are the removal of ethanol (Izquierdo-Gil and Jonsson 2003); the removal of ammonia (El Bourawi et al. 2007) or VOCs from water, like toluene, benzene, etc. (Couffin et al. 1998); and the recovery of aroma compounds (Soni et al. 2008; Diban et al. 2009).

Table 1 summarizes the main applications of VMD.

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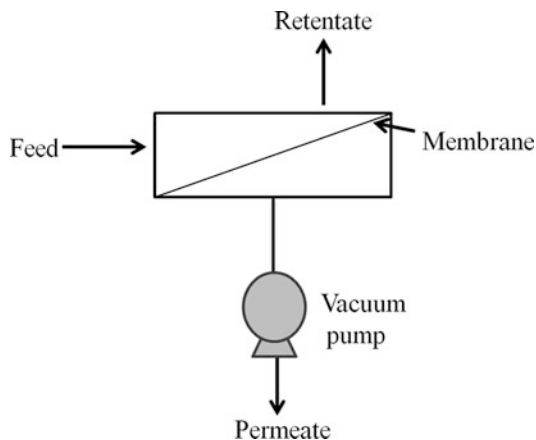
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Vacuum-Driven Pervaporation

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Pervaporation is a concentration-driven membrane process in which a feed liquid mixture is directly in contact with the “active selective layer” of the membrane, while the permeate in a vapor phase is constantly removed from the other side. The driving force is represented by a gradient in the partial vapor pressure that creates a chemical potential gradient in the liquid phase, which is



Vacuum-Driven Pervaporation, Fig. 1 Vacuum-driven pervaporation

responsible for the selective sorption of one feed component into the membrane matrix, its subsequent diffusion through the membrane, and its final desorption into the permeate side. In pervaporation, in order to maintain a vapor pressure difference, any of the following, i.e., a sweeping carrier gas, a vacuum downstream pressure, or a temperature difference, can be used. By applying vacuum to the downstream side, for instance, a decrease in the chemical potential gradient is obtained and a selective mass transfer can be induced (Vallieres and Favre 2004).

At small scale a vacuum pump is often used in order to get a low vapor pressure. At industrial scale, on the contrary, the dimensions required for a vacuum pump would be prohibitive to reach. An alternative is represented by the condensation of the permeate vapor that spontaneously creates a vacuum in the permeate side (Baker 2004) (Fig. 1).

Vacuum, as opposed to sweeping gas, does not require any further separation from the sweeping gas; moreover, the vapors can be recovered by condensation, and in many cases, its use can simplify the overall process.

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Vapor Permeation

► Alcohol Removal by Membrane Operations

Vapor Plasma Membrane Treatment

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Plasma processes (Yasuda 1985; d'Agostino 1990; Biederman and Osada 1992; Inagaki 1996) were initially developed for microelectronics in the 1950s. They represent a clean (producing few or not effluents) and also extremely flexible technology whose basic equipment, well adapted to automation, makes it possible to achieve goals as various as singular in terms of specific properties of use; their costs of operation are moreover relatively weak. Based on these advantages, they are used today in many fields of the materials chemistry (in particular the membranes field) even if their industrialization still remains not very developed, because of the high cost of the equipment necessary to their implementation and of a certain conservatism of the industrialists reticent to introduce this new technology, however so promising.

Defined by Crookes in 1879 as the fourth state of the matter, a plasma is a partially ionized and overall neutral medium generated by the application of an electric field to a gas phase at low pressure (<10 Torr). The energy of the applied electric field is transferred to free electrons which collide with the gas molecules. Such inelastic impacts make electrons achieve enough energy (up to 50 eV) to induce the ionization of gas molecules. Such ionized species (acquiring energies typically in the range of 0–2 eV) initiate a

high number of complex reactions (ionization, excitation, neutralization, recombination, deexcitation, etc.) constituting what is called a glow discharge. A glow discharge implies a high variety of species: electrons, negative and positive ions, radicals, neutral atoms and molecules, and also photons (emitted by radiative deexcitation) whose mixture constitutes the plasma state. A plasma is essentially characterized by its energy and its electronic density. Depending on the values of both microscopic parameters, different kinds of natural or artificial plasmas can be distinguished, being classified in two categories: hot plasmas and cold plasmas. Artificial plasmas, generated by a low frequency (25–450 kHz), radio frequency (1–500 MHz), or microwave (500 MHz–some GHz) continue or alternative discharge at rather low pressure (10–2–10 Torr), are cold plasmas. Cold plasmas are characterized by energy and electronic density equal to 1–10 eV and $1,010\text{ cm}^{-3}$, respectively. Their ionization degree is lower than 10^{-3} so that the gas phase is mainly made up of neutral species in an excited state (radicals). A characteristic of these plasmas is the absence of thermodynamic balance between the electronic temperature (several thousands of degrees) and that of gas (near to the ambient).

The interaction between a cold plasma and a material placed within it (substrate) results in several types of effects occurring simultaneously or consecutively. Four major effects are generally distinguished: plasma etching, plasma functionalization, plasma cross-linking, and/or formation of a deposit on the surface of the substrate (PECVD/plasma polymerization). The prevalence of one of these effects on the others is directly related to the nature of the gas subjected to the electric discharge. In the case of plasmas involving noncondensable gases (monoatomic or diatomic gases), the three principal effects are etching, functionalization, and cross-linking; the substrate undergoes surface modifications only. In the case of plasmas involving condensable gases (organic, inorganic, or organometallic compounds), the dominating effect is the formation, on the surface of the substrate, of a deposit made up of a three-dimensional matrix formed from fragments of the reagent gas combined in a random way. The

related plasma process is called plasma-enhanced chemical vapor deposition (PECVD) or plasma polymerization in the particular case of gases of organic compounds.

For details about plasma treatment applied to membrane materials, see the articles entitled “plasma etching,” “plasma functionalization,” “PECVD,” “plasma polymerization,” “plasma membrane,” and “plasma polymerized membrane.”

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Vapor Pressure–Temperature Relationship

► Antoine Equation

Variable Volume Diafiltration

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Variable volume diafiltration (VVD) is a type of batch diafiltration process in which fresh diluant is continuously added to the feed tank at a rate that is proportional but less than the permeate flow. This causes a gradually diminishing feed volume and a simultaneous concentration of macrosolute and removal of microsolutes. Thus, this technique is more than a simple diafiltration in its strict and traditional sense since it is not designed only to

wash out the microsolutes but also enables the concentration of the process liquor within a single-step operation.

The process is controlled by measuring the permeate flow and adjusting the diluant flow accordingly with a control valve. The proportionality factor α , that is, the ratio of diluant flow $d(t)$ to permeate flow $q(t)$, is then kept constant such that $0 < \alpha < 1$.

For a given process, in which the macrosolute concentration is to be increased from $c_1(0)$ to $c_1(t_f)$, while the microsolutes concentration is to be reduced from $c_2(0)$ to $c_2(t_f)$, the proportionality factor α can be calculated by the following formula (Tekić et al. 2002):

$$\alpha = \frac{R_1 \ln \frac{c_2(0)}{c_2(t_f)} + R_2 \ln \frac{c_1(t_f)}{c_1(0)}}{\ln \frac{c_1(t_f)}{c_1(0)} + \ln \frac{c_2(0)}{c_2(t_f)}}$$

where R_1 and R_2 are the rejection of macrosolute and microsolutes, respectively, and are assumed to be constants throughout the filtration process.

Variable volume diafiltration has been originally proposed by Jaffrin and Charrier (1994) for a UF/DF process for albumin production from human plasma. The proposed technique, however, has found to be suboptimal for that particular application as concluded by an in-depth mathematical analysis based on optimal control theory (Paulen et al. 2011).

Although variable volume diafiltration could offer substantial advantages over constant volume diafiltration in terms of water usage (Krstić et al. 2004), it compares unfavorably with an optimally run traditional diafiltration process (Foley 2006a). As a further improvement, Foley (2006b) has suggested that the performance of variable volume diafiltration under certain circumstances can be enhanced in terms of diluant consumption and operational time by including a pre-concentration step.

Variable volume diafiltration is a relatively new concept, and only a few experimental investigations on its performance are available in the literature. These include, for example, ethanol removal from albumin (Jaffrin and Charrier 1994), fructooligosaccharide separation

(Li et al. 2004), and whey desalination (Román et al. 2011).

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and cross-flow velocity, respectively, in dead-end and cross-flow systems. However, shear rate can also be generated by moving the membrane surfaces instead of the surrounding fluid or by moving a mass very near to the membrane surface. This type of technique is categorized as dynamic filtration systems (DFSs), also called shear-enhanced filtration. A summary of the existing DFSs is given in Table 1.

Most DFSs decouple the generation of surface shear rate from the feed velocity. Thus in theory, the mechanical energy is more efficiently directed toward the membrane surface by membrane or liquid movement near the membrane surface. Ideally, these systems offer reduced energy consumption and more effective and efficient fouling minimization. Only a limited number of reports mention the weakness of DFS systems. General energy calculations in comparison to conventional dead-end or cross-flow systems are scarce, making it difficult to verify the claim of energy savings during operation compared to conventional membrane filtration systems. These systems also have other drawbacks, such as apparatus complexity, high tendency of the apparatus to breakdown at the moving parts, and a low packing density, leading to high costs per membrane area (Jaffrin 2008). The latter seems to be the main restriction to commercialize these technologies.

Vibrating membranes are categorized as DSFs. They are known as an effective technique to provide shear rate on the membrane-feed interface in order to control membrane fouling. It is relatively new and only few versions exist and have been tested for different applications, mainly for activated sludge filtration in membrane bioreactor (MBR) applications. The vibrating membranes include the vibrating hollow fiber modules (VHFM) and magnetically induced membrane vibrations (MMV). In the VHFM, the membrane module consists of hollow fiber membranes placed vertically. The skin layer is located at the outside of the fibers. The membrane modules are vibrated in a vertical motion at different frequencies (0–30 Hz) and different amplitudes (0.2–4 cm) (Beier et al. 2006; Genkin et al. 2006). The oscillation of

Vertically Aligned Carbon Nanotube

► Aligned Carbon Nanotube

Vibrating Membranes

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Applying shear at the membrane surface is the most efficient way to control membrane fouling in a membrane filtration process (Jaffrin 2008). It is traditionally provided by coarse bubble aeration

Vibrating Membranes, Table 1 Summary of existing DFSs (Beier 2008)

System	Description	Application and commercial system
VSEP	Membrane is oscillated at high frequency (around 60 Hz) in parallel motion relative to the flat-sheet membrane surface. The vibration energy focuses shear waves directly at the membrane surfaces repelling solids and foulant, while increasing the permeate rates.	UF, NF, RO (Pall Corp, New Logic)
RD	Filtration module contains a disk, rotating around an axis, while the flat-sheet membrane is stagnant. The module is sometimes installed with addition of vanes.	MF, UF, NF (Pall Corp)
CR	Filtration module consists of a rotating motor sandwiched between stagnant flat-sheet membranes.	MF, NF (Mesto Papper)
RM	The flat-sheet membrane is mounted onto a rotating hollow disk. The rotation of the disk creates a centrifugal force across the membrane surface.	MF, UF (SpinTek)
CMS	The apparatus consists of a membrane head at the end of a rotor arm, containing a plate and frame stack of membranes. It is placed inside housings.	RO
MSD	The filtration system consists of two parallel hollow shafts rotating at the same speed, each bearing six ceramic membrane disks.	MF (Westfalia Separator)

RD rotating disk system, *CR* cross-rotational filter systems, *RM* rotary membrane systems, *CMS* centrifugal membrane separation systems, *MSD* multishaft disk systems, *UF* ultrafiltration, *NF* nanofiltration, *RO* reverse osmosis, *MF* microfiltration

the membrane in a VHFM system can also be performed in the transverse direction, which also proved to maintain good performance. This technique has proven to significantly increase the

achievable fluxes both for yeast broth and activated sludge filtration (Beier and Jonsson 2007; Gomaa et al. 2011).

In MMV, the membrane (normally flat-sheet) is fixed onto a vibration frame that is directly connected to an engine. The engine vibrates the frame via a pull-and-push mode and the vibration is derived from a programmable sonic device (Bilad et al. 2012; Mezohegyi et al. 2012). Like in the DSF systems, only the liquid-membrane interface experiences shear stress and not the bulk liquid, thus minimizing energy consumption and limiting the impact of the movement on the bulk feed. The movement orientation of the vibrating parts faced the narrow face of the module in order to both prevent the bumping of liquid onto the membrane and minimize the associated energy dissipation.

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VOC Recovery

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Synonyms

Organic vapor recovery

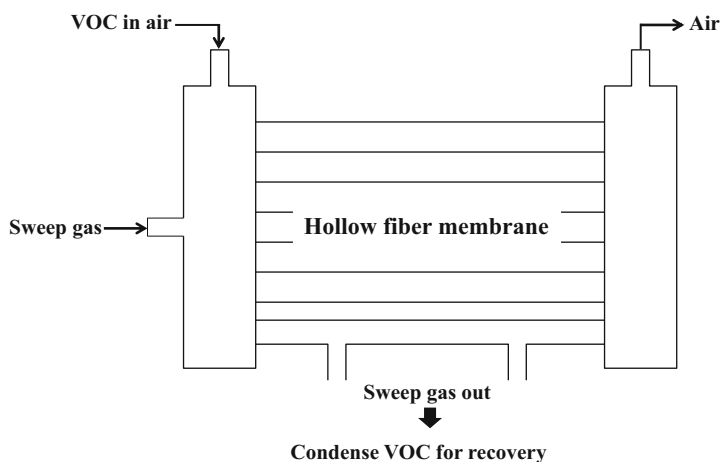
Many industrial processes handling organic solvents emit volatile organic compounds (VOCs). These VOCs not only cause environmental pollution but also represent an economic loss. The VOC recovery has become a big issue that needs to be addressed. Traditional techniques for VOC removal include carbon adsorption, condensation, and absorption, and none is efficient enough to meet every need. Membrane separation has developed into an important technology for separating VOCs and other gaseous air pollutants from gas streams. The membrane technology utilizes a polymeric membrane that is more permeable to condensable organic vapors, such as C_3 hydrocarbons and aromatics, than it is to noncondensable gases such as methane, ethane, nitrogen, and hydrogen. Because the technology concentrates the VOC gas stream, it can be used with a condenser to recover the VOC. It is best suited for

relatively low-flow streams containing moderate VOC concentration (Fig. 1).

The typical overall VOC recovery process consists of two steps: (1) compression and condensation and (2) membrane separation. A mixture of vapor and air is compressed. The compressed mixture is cooled and condensed vapor is recovered. Uncondensed organics are separated from the gas stream and concentrated in the permeate by the membrane. The treated gas is vented from the system and the permeate is drawn back to the compressor inlet. The polymeric membrane consists of a layer of nonwoven fabric that serves as the substrate, a solvent-resistant microporous support layer for mechanical strength, and a thin-film selective layer that performs the separation. It is manufactured as flat sheet and is wrapped into a spiral-wound module. Membranes are best suited for treating VOC streams that contain more than 1,000 ppmv of organic vapor where recovered product has value. Typical VOC recovery using membrane separation ranges from 90 % to 99 % and can reduce the VOC content of the vented gas to 100 ppmv or less. In Table 1, VOCs that can be captured with the membrane separation technique are listed.

The separation of VOCs from nitrogen by composite hollow fiber membranes is reported. Microporous hollow fiber membranes were spun from poly(vinylidene fluoride) (PVF₂) using the phase inversion method, and the hollow fibers were coated with a thin layer of poly(ether block

VOC Recovery,
Fig. 1 Recovery
membrane model for VOCs



VOC Recovery, Table 1 Typical VOCs

Acetaldehyde	BFC-134a
Acetone	Hexane
Acetonitrile	Methanol
Carbon tetrachloride	Methyl chloroform
CFC-11	Methyl isobutyl ketone
CFC-12	Methylene chloride
CFC-113	Propylene oxide
Chlorine	Styrene
Chloroform	Toluene
Ethylene dichloride	Trichloroethylene
Ethylene oxide	Vinyl chloride
HCFC-123	Xylenes

amide) (PEBA), thereby forming composite membranes. PVF₂ was chosen as the substrate material because of its excellent thermal and chemical stabilities and good mechanical strength, and PEBA was selected as the active separating layer because of its good permselectivity and film forming properties. The membranes were tested for the recovery of representative VOCs including hexane, heptane, and cyclohexane, which are the main components of gasoline, and dimethyl carbonate, ethanol, methanol, and methyl *t*-butyl ether that are the oxygenates and octane number enhancers of gasoline. The separation of gasoline vapor from nitrogen was also investigated under various operating conditions (e.g., feed concentration, operating temperature). The PEBA/PVF₂ composite hollow fiber membranes were effective for the separation of hydrocarbon vapors from nitrogen.

PDMSvi was prepared from divinyl-terminated poly(dimethylsiloxane), platinum-divinyltetramethylsiloxane complex, oligosilylstyrene, and hexane. PDMSvi–Al₂O₃ composite hollow fiber membrane was developed by coating a PDMSvi-oligo film on the outer surface of an Al₂O₃ hollow fiber porous substrate. Microstructures of the composite membranes were examined using scanning electron microscopy (SEM), displaying a uniform PDMSvi-oligo coating layer, free of defects with a thickness of around 15 µm. Such composite hollow fiber membranes are suitable for VOC recovery from waste gas streams because of their high chemical stability. The separation performances of the

PDMSvi–Al₂O₃ composite hollow fiber membrane were studied using chloroform in N₂ as a test vapor mixture. By analyzing the experimental data obtained at various conditions with a mathematical model derived, the permeabilities of chloroform and nitrogen in the PDMSvi polymer membrane were obtained. The effects of temperature, feed flow rate, vacuum pressure on the permeate side, and feed concentration on the chloroform recovery were also investigated both experimentally and theoretically. A high chloroform recovery was recognized (Liu et al. 2005).

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Volatile Organic Compounds (VOCs)

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Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary, room-temperature conditions. Their high vapor pressure results from a low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air. Many VOCs are dangerous to human health or cause harm to the environment. VOCs are numerous, varied, and ubiquitous. They include both human-made and naturally occurring chemical compounds. VOCs play an important role in communication between plants. Volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Concentrations

Table 1 Various volatile organic compounds

Compounds	bp (°C)	VOCs
Very volatile organic compounds (VVOC)	0 ~ 50–100	Propane, butane, methyl chloride etc.
Volatile organic compounds (VOC)	50–100 ~ 240–260	Formaldehyde, toluene, acetone, ethanol, isopropanol, etc.
Semivolatile organic compounds (SVOC)	240–260 ~ 380–400	Insecticide, plasticizer

The emitted VOCs have to be removed by any method. Membrane separation technology is effective for the removal of VOCs in air (see chapter ► [VOC recovery](#))

of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. VOCs are emitted by a wide array of products numbering in the thousands. Examples include paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings, office equipment such as copiers and printers, correction fluids and carbonless copy paper, graphics and craft materials including glues and adhesives, permanent markers, and photographic solutions. Organic chemicals are widely used as ingredients in household products. Paints, varnishes, and wax all contain organic solvents, as do many cleaning, disinfecting, cosmetic, degreasing, and hobby products. Fuels are made up of organic chemicals. All of these products can release organic compounds while you are using them and, to some degree, when they are stored. Table 1 is listed some VOCs in WHO.

Volume Concentration Factor

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The aim of any batch membrane filtration process is to reduce the retentate volume, thus increasing

the concentration of a key molecular or particulate species.

The volume concentration factor is simply the ratio of the initial solution volume to the final solution volume, i.e., V_0/V_f . It is usually denoted by the abbreviation VCF.

For a solute or particle that has a rejection coefficient of 1.0, the increase in concentration during batch operation is given by

$$c_f/c_0 = V_0/V_f$$

Therefore,

$$c_f = c_0 VCF$$

If the solute has an arbitrary and constant apparent rejection coefficient of σ , one gets

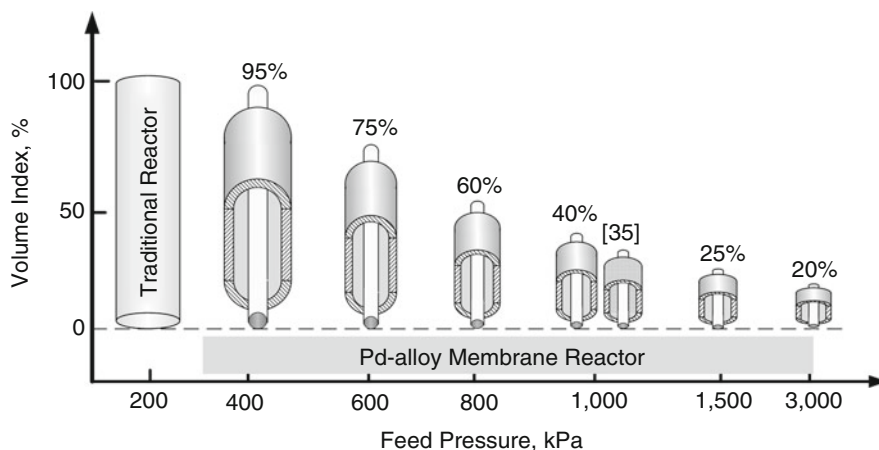
$$c_f = c_0 VCF^\sigma$$

Volume Index

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The use of membrane reactors has several advantages, the most important of which is related to the gain in terms of conversion, with better material exploitation and plant size reduction. In order to compare membrane performance with that of conventional operations, different parameters were proposed (Criscuoli and Drioli 2007).

Behind them, the volume index is a new index, introduced (Brunetti et al. 2007, 2011a, b, 2012a, b; Barbieri et al. 2011) as an important parameter when installing new plants, which must be characterized by low sizes and high productivities. In particular, it is an indicator comparing the membrane reactor (MR) volume with that of a



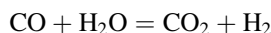
Volume Index, Fig. 1 Volume index as a function of feed pressure for an equimolecular $\text{H}_2\text{O}:\text{CO}$ mixture. Furnace temperature = 280 °C. Set CO conversion 90 % of the TREC (Brunetti et al. 2007)

traditional reactor (TR) one, in order to achieve a set conversion, Eq. 1:

$$\text{Volume Index} = \frac{\text{Volume}_{\text{reaction}}^{\text{MR}}}{\text{Volume}^{\text{TR}}}_{\text{Set Conversion}} \quad (1)$$

The volume index ranges from 0 to 1: a low volume index means that the reaction volume for a membrane reactor to reach the set conversion value is much lower with respect to that required by a conventional reactor. Therefore, the necessary catalyst weight in the membrane reactor is significantly reduced.

The water-gas shift reaction can be considered as an example:



The volume index is a decreasing function of CO feed pressure, at a set temperature (Fig. 1): when an equimolecular ($\text{H}_2\text{O}:\text{CO} = 50:50$) mixture is fed into the reactor at 1500 kPa and a final conversion of about 80 % (corresponding to 90 % of the *Traditional Reactor Equilibrium Conversion*) is considered, the MR volume is 25 % of that of a TR and the volume index is equal to 1/4. With a high feed pressure, more H_2 permeates through the membrane, causing the reaction to shift toward further CO conversion. As a consequence a lower catalyst amount is required to achieve a set conversion.

When the mixture is fed at 600 kPa, the reaction volume of the membrane reactor is 75 % of the traditional reactor one, for the same CO conversion.

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Wash Water in Diafiltration

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In the context of ► [diafiltration](#), wash water is simply another term for diluent.

This is the water used to replace impure solvent while retaining the desired product. A typical example might be the washing of a cell suspension prior to cell disruption to release an intracellular product.

The typical way of doing this would be to subject the cell suspension to batch crossflow microfiltration while adding wash water at a rate that exactly balances the filtrate (► [permeate](#)) flow rate. Thus, the cells are retained, but the impure liquid in which the cells are suspended is gradually displaced by wash water.

Water Competitive Diffusion

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Background: Increasingly stringent recycled water quality standards and environmental

regulations force industries to look out for attractive green technologies involving membranes. Appropriate selection and utilization of membrane process over a vast range of applications requires fundamental knowledge of transport mechanisms occurring within the membrane. To describe the transport mechanisms, several mathematical models have been developed that are divided into two categories: phenomenological and mechanistic models. In phenomenological model, the membrane is viewed as a “black box” through which the feed components pass selectively with a certain driving force, and the membrane performance is defined in terms of solute passage and water flux, whereas the concentrations in the feed and permeate sides are related by empirical equations. Mechanistic transport models relate the membrane performance to physical parameters such as pore structure, solute size, and chemical properties like mode and energy of interaction between the membrane and feed components. In dense membranes, the solution-diffusion and pore flow models are mostly followed. Depending upon the nature of feed components and quantity required to be separated, the membrane type is selected. Hydrophilic membranes are suitable for retaining organic component, whereas hydrophobic barriers are desirable for separating small amount of solvent from water.

Competitive sorption is a special characteristic taking birth from the relative hydrophilicity of the membrane. Due to the water-loving nature of the

membranes or owing to the repulsive force of the membranes to water other solutes, a layer of pure water gets adsorbed onto the membrane surface on the basis of size exclusion. Pervaporation, reverse osmosis, and forward osmosis are membrane processes wherein water sorption occurs along with ultrafiltration and microfiltration. The ion exchange membrane used in electrodialysis and the solid polymer electrolyte which conducts protons in fuel cell also undergo competitive water sorption.

Pervaporation (PV): Pervaporation is a unique membrane technique which has found considerable importance due to its efficiency in liquid mixture separation, which cannot be performed by conventional distillation processes. Examples include azeotropic mixtures, thermally unstable and thermally sensitive products, and mixtures possessing components with close boiling points (Sunitha et al. 2013). In this process a very small amount of feed solution is vaporized, using both polymeric and inorganic membranes resulting in low energy consumption. Membrane performance is based on the phenomena of preferential sorption which allows selective components to get preferentially sorbed on the membrane surface followed by diffusion through the pores and finally desorption on the permeate side as vapor. Depending on the hydrophilicity of the membrane, water from the solution gets sorbed on the membrane surface, preventing other solutes from permeating. Presently, inorganic membranes have been proven to be attractive alternatives since they have superior thermal resistance and mechanical strength as described by Sommer and Melin (2005). Kita et al. (1995), Kondo et al. (1997), and Li et al. (2001) separated the azeotropic mixture of tetrahydrofuran (THF)/water by using different types of zeolitic membranes, namely, A-type, Y-type, MOR, and ZSM-5. Gallego-Lizon et al. (2002) used polymeric, microporous silica and NaA-type zeolite for the dehydration of *t*-butanol/water mixtures obtained and reported high flux and selectivity values due to preferential sorption of water which competes against the corresponding organics for permeation.

$$\text{Process selectivity} = \frac{(X_{H_2O, perm}/X_{i, perm})}{(X_{H_2O, feed}/X_{i, feed})} \quad (1)$$

$X_{H_2O, Perm}$ = water concentration in permeate (wt. %)

$X_{H_2O, Feed}$ = water concentration in the feed (wt. %)

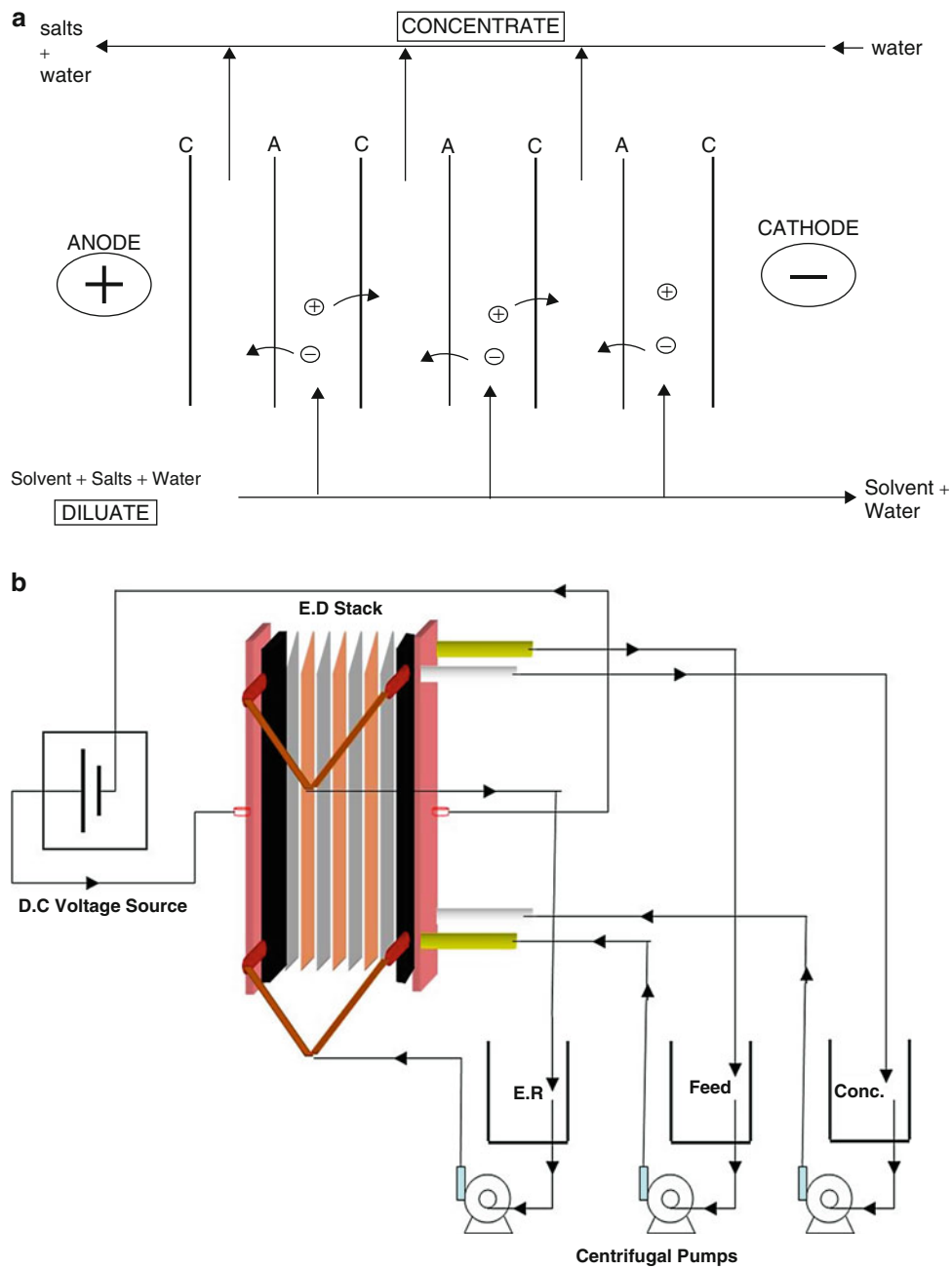
$X_{i, Perm}$ = concentration organic component in permeate (wt. %)

$X_{i, Feed}$ = concentration organic component in the feed (wt. %)

Electrodialysis (ED): ED is a process where water gets sorbed competitively to swell the ion exchange membrane and allow easy mobility of ionizable species. The principle of electrodialysis is displayed in Fig. 1a, and the experimental setup is illustrated in Fig. 1b. The laboratory setup of ED process is shown in Fig. 1c. In ED, water sorption allows transport of ionic moieties through the swollen portions of the membrane which promote conduction of both cations and anions retaining organic solvents and other solutes. Some examples include removal of sodium azide from DMSO/water mixtures to enable distillation which is otherwise not feasible in the presence the explosive azide (Ravikumar et al. 2013).

Figure 1a reveals the alternate arrangement of cation and anion exchange membranes for removal of ionizable species like salts, acids, and alkalis from aqueous solutions, while Fig. 1b provides illustration of a typical ED experimental setup wherein the ions move through a membrane stack which is subjected to DC voltage through electrodes on both sides. With time, the dilute gets depleted of ionizable compounds which get transferred to the concentrate compartments while a third solution is provided to rinse the electrodes, remove air gap, and collect by-products.

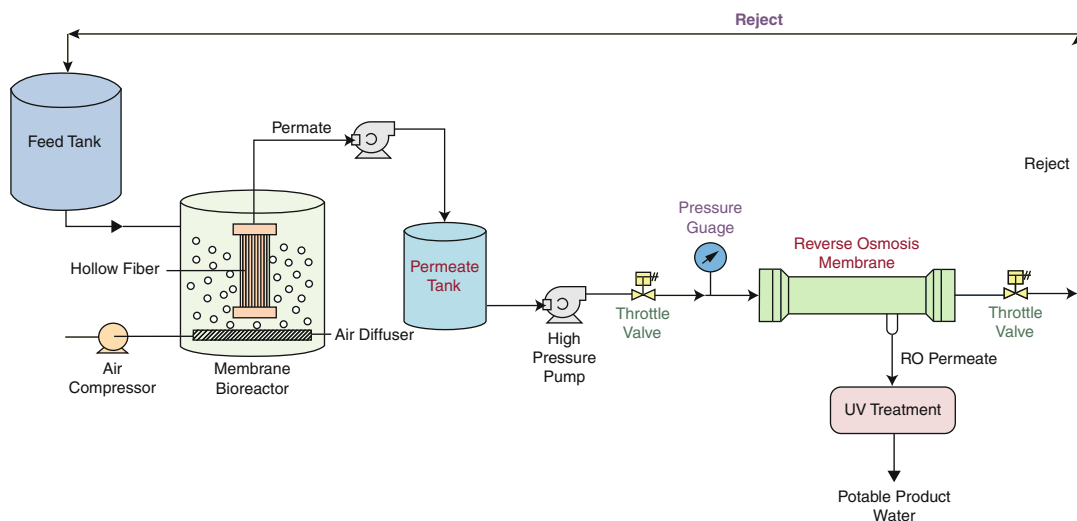
Membrane bioreactor (MBR): MBR comprises of a conventional activated sludge process coupled with membrane separation to retain the biomass effectively, producing a clarified and disinfected permeate water suitable for reuse. Significant benefits of MBR include complete



Water Competitive Diffusion, Fig. 1 (a). Principle of ED. (b). Experimental setup of ED

retention of particulate matter, high purity of dissolved organics, and stable operation performance. The water present in the effluent is able to pass through the pores of the membranes while most particulates and bacterial cells are retained in

the bioreactor which is linked to the pore size distribution of the membranes. The types of membranes used are different depending on the size of the contaminants of the treatment process. Typically, for contaminants with particle size ranging



Water Competitive Diffusion, Fig. 2 Aerobic MBR combined with RO for enhanced water purity

from 100 to 1,000 nm, MF membranes are used for removing suspended particles, UF for particle size of 5–100 nm excluding both bacteria and virus, and NF for particles with size 1–5 nm retaining bivalent and multivalent dissolved salts. The MBR design is of two types, where the membrane is either operated under direct pressure or vacuum. This can be done either by placing the membrane inside the tank in submerged mode or can be configured externally in sidestream mode of filtration. In submerged MBR system, the feed wastewater and the biomass are both passed through the membrane that is operated at a pressure lower than atmospheric, and a vacuum pump is used to draw the permeate out while the concentrated sludge is recycled back to the reactor. In the sidestream configuration, the membrane is placed in an external loop separated from the bioreactor, and a pump forces the biomass containing water under direct pressure in a cross-flow mode into the membrane module to generate permeate on the other with recycle of biomass to the reactor. Membrane filtration occurs either in aerobic or anaerobic configuration where oxygen acts as an important medium for biomass growth in the aerobic process while the anaerobic process is carried out in the absence of oxygen.

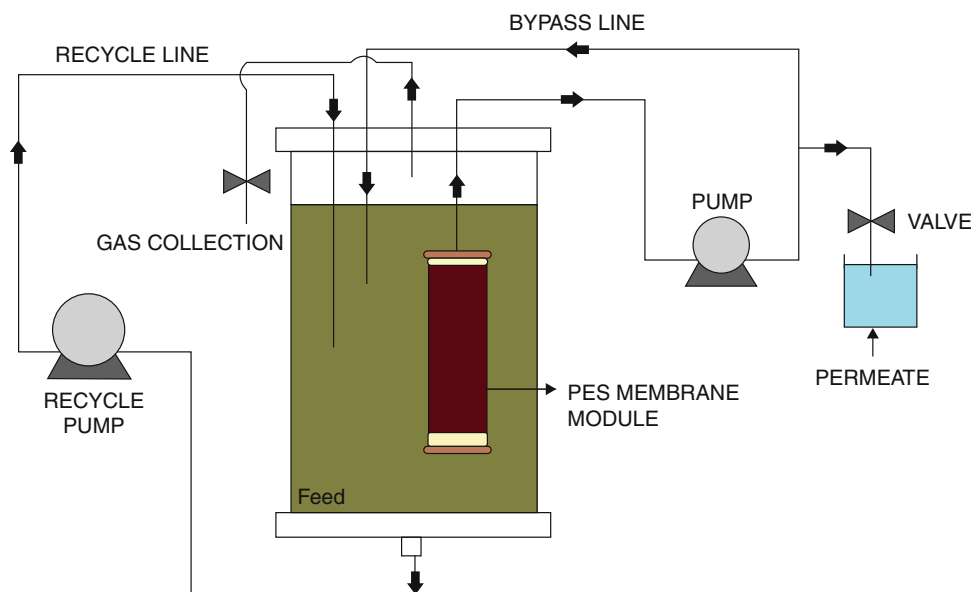
Aerobic membrane bioreactor: This type of MBR depends on aeration within the system

providing required oxygen transfer for growth of the biomass and mixing in the reactor. As shown in Fig. 2, the rising bubbles created by an air diffuser provide turbulent cross-flow over the surface of the membrane to maintain flux and reduce buildup of materials on the barrier, thereby increasing the operational cycle of the system.

Anaerobic membrane bioreactor: This process is operated without oxygen, and the anaerobic biomass degrades the particulate matter in the wastewater converting a part of it into biogas and using a membrane to provide complete solid-liquid separation.

With the advantage of biomass retention, these reactors are suitable to treat high-strength wastewaters and could also operate at higher COD/BOD loading rates (Germain et al. 2007). Figure 3 represents the anaerobic bioreactor where the membrane is immersed in a tank and operated under vacuum mode to withdraw permeate.

Forward osmosis (FO) and reverse osmosis (RO): Forward osmosis is a process which uses a semipermeable membrane for the transfer of water molecules due to the difference in osmotic pressure across the membrane allowing passage of water, rejecting solute molecules or ions. Some of the applications include sea- and brackish-water desalination and processing of



Water Competitive Diffusion, Fig. 3 Anaerobic MBR

pharmaceuticals besides concentration of fruit juices, dairy products, and beverages.

RO is a combination of interfacial phenomenon and fluid transport under pressure through capillary pores. In this process pure water is passed through a semipermeable membrane under the influence of hydrostatic pressure with simultaneous removal of impurities, organic contaminants, and salts. The two types of membranes used for reverse osmosis process are thin-film composite polyamide and cellulose acetate. Properties like water flux, rejection, and physiochemical characteristics are different for different membranes (Gullinkala et al. 2010). The thin-film composite (TFC) membrane has an upper ultra-thin active layer that mostly consists of cross-linked polyamide, polyester, polyurea, or polyetherurea which are supported on a porous polysulfone support with a grid of polyester fibers for mechanical stability at the bottom (Petersen 1993). TFCs exhibit high permselectivity to water and low resistance to mass transfer during osmotic flow due to the enhanced hydrophilicity nature. To evaluate RO system performance, water flux and % salt rejection of the membrane are determined experimentally. Water flux is measured as the volume (L) of permeate collected on a certain

period of time (h) per square meter per hour (m^2) of membrane area (L/m^2h) and calculated through the following equation:

$$J_v = \frac{Q}{AX\Delta t} \quad (2)$$

where J_v is the volumetric permeate water flux, A is the effective area of the membrane for permeation, and Q is the volume of permeation over a time interval Δt . Salt rejection is evaluated by the following equation:

$$\%R = \frac{C_f - C_p}{C_f} \times 100 \quad (3)$$

C_p and C_f are salt concentrations in permeate and feed, respectively. To understand the transport mechanism of RO process, different mathematical models are described which can be classified into three categories: (i) irreversible thermodynamics model/Kedem Katchalsky and Spiegler Kedem models; (ii) nonporous membrane models, viz., solution-diffusion, solution-diffusion-imperfection, and extended solution-diffusion models; and (iii) pore flow models like finely porous, preferential sorption-capillary flow

and surface force-pore flow models. Here, our focus is on the pore flow model.

Pore Flow Models

Preferential Sorption-Capillary Flow Model

This is a model proposed earlier by Sourirajan (1970) and is assumed that the mechanism of separation is carried out by both surface phenomena and fluid transport through pores in the RO membrane. As in the case of PV, as mentioned above, this model also assumes that chemical properties of the membrane attract the solvent and repel the solutes present in the feed solution. A layer of the pure solvent gets preferentially sorbed on the surface of the membrane and subsequently within the pores of the membrane. Solvent transport is forced through the capillary-like pores under pressure. According to this model the water flux is given by

$$N_w = A[\Delta P - \{\pi(X_F) - \pi(X_P)\}] \quad (4)$$

where A is the pure water permeability constant of the membrane, and $\pi(X)$ represents the osmotic pressure of the feed with solute mole fraction X .

The solute flux is expressed as

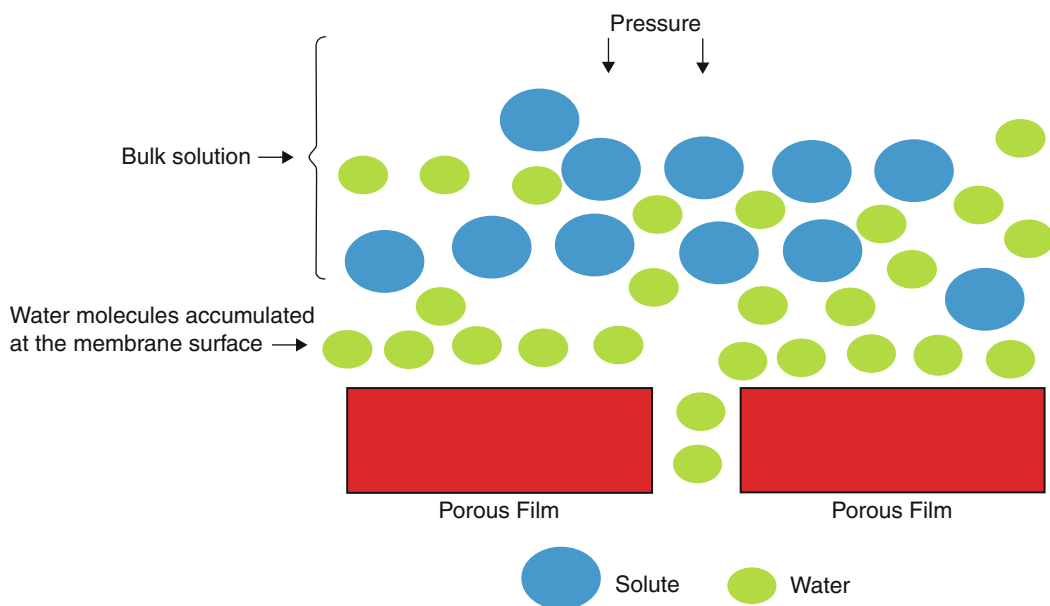
$$N_s = \frac{D_{SP}K_D C_T}{\delta} (X_F - X_P) \quad (5)$$

where K_D is the distribution coefficient of the solute between the feed and the pores of the membrane, and D_{SP} is the diffusivity of the solute within the membrane pore. Solute rejection is given by

$$\frac{1}{R} = 1 + \frac{D_{SP}K_D C_T}{\delta} \times \frac{1}{A[\Delta P - \{\pi(X_F) - \pi(X_P)\}]} \quad (6)$$

These equations were used to analyze transport for a large number of solutes and membranes by Sourirajan and Matsuura (1985). But the drop in water flux and solute rejection caused by presence of dilute organics is not adequately described by these equations.

The surface of the membrane in contact with the solution has a preferential affinity for water and repulsion toward the solute. According to the capillary flow model, solutes move through the membrane by solution-diffusion, advection, or both (Chanda and Roy 2008). Figure 4 shows



Water Competitive Diffusion, Fig. 4 Phenomenon of competitive water sorption in RO

Water Competitive Diffusion, Table 1 Literature review of processes wherein membranes undergo competitive water sorption

S. No.	Membrane process	Membrane type	Water selectivity	Permeation rate (cm/h) $\times 10^2$	%Water in permeate	Reference
1	PV	PSf/PVDF	19.0	0.5	95	Mulder et al. (1983)
2	PV	PAN/Nylon6	9.0	2.0	90	Mulder et al. (1983)
3	PV	PVDF support	1.0	20	50	Mulder et al. (1983)
4	PV	PAN	70	0.15	98.6	Mulder et al. (1983)
5	PV	PDMS	0.3	1.75	21	Mulder et al. (1983)
6	PV	PVDF	1.0	4.5	50	Mulder et al. (1983)
7	PV	PSf	332	0.04	99.7	Mulder et al. (1983)
8	PV	CA	2.0	11.3	66.9	Mulder et al. (1983)
9	FO	TFC	NA	NA	99	Greg et al. (2011)
10	ED	AEM	NA	1.4	30	Jaime et al. (2008)
11	ED	CEM	NA	2.4	37	Jaime et al. (2008)
12	ED	BP	NA	1.12	25	Jaime et al. (2008)

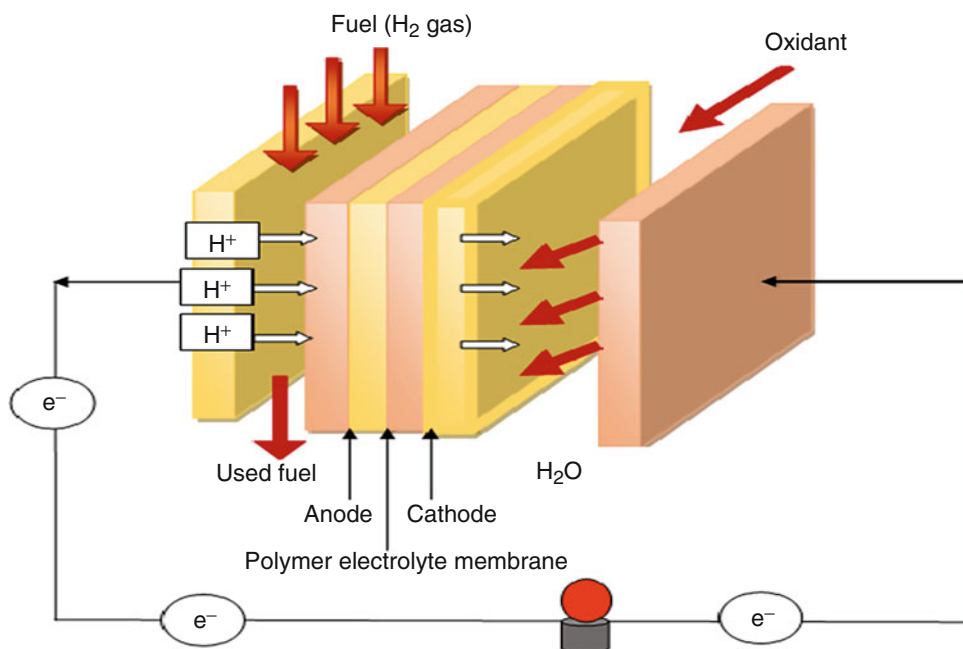
CA cellulose acetate, PAN polyacrylonitrile, PSf polysulfone, PDMS polydimethylsiloxane, BP bipolar membrane, AEM anion exchange membrane, CEM cation exchange membrane, PVDF polyvinylidene fluoride, PSf, NA not available

the detailed mechanism of water competitive sorption in RO process. This separation process is a function of surface chemistry of the membrane as well as the way water is transported through the membrane. The solutes having higher hydration radii will be rejected by the adsorbed water, but other smaller solute molecules can diffuse through the membrane pores.

Compounds which exist as cations, anions, or zwitterions, depending upon the solution pH, can be separated by a unique mechanism from fermentation broths. Ion exchange membranes are modified hydrophobic polymers which contain small volume unsuitable for separation of large organic molecules besides possessing inherent disadvantages like high energy consumption, organic fouling, etc.

To minimize these problems, ion exchange membranes having high proton conductivity, low electrical resistance, high water sorption, and permselectivity are prepared. Swelling property

of these membranes has been investigated with different solvent-water mixtures containing ionizable solutes. Therefore, Kang et al. (2002) prepared a cation exchange membrane which had a high water-swelling property with significant conductivity and low electric resistance, which was poly(vinyl alcohol) (PVA)/poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA) for separation of large molecular cations of amino acids. The electric resistance of the PVA/PSSA-MA membrane is lower than commercial membranes for easier transport of large molecular cations due to the relatively higher free volume present in the membrane structure. As a result, PVA/PSSA-MA membranes show better separation efficiency in the presence of water since their permeable matrix allows the large cation molecule to easily pass through the negatively charged barrier. Table 1 represents the literature review of processes involving water competitive sorption.

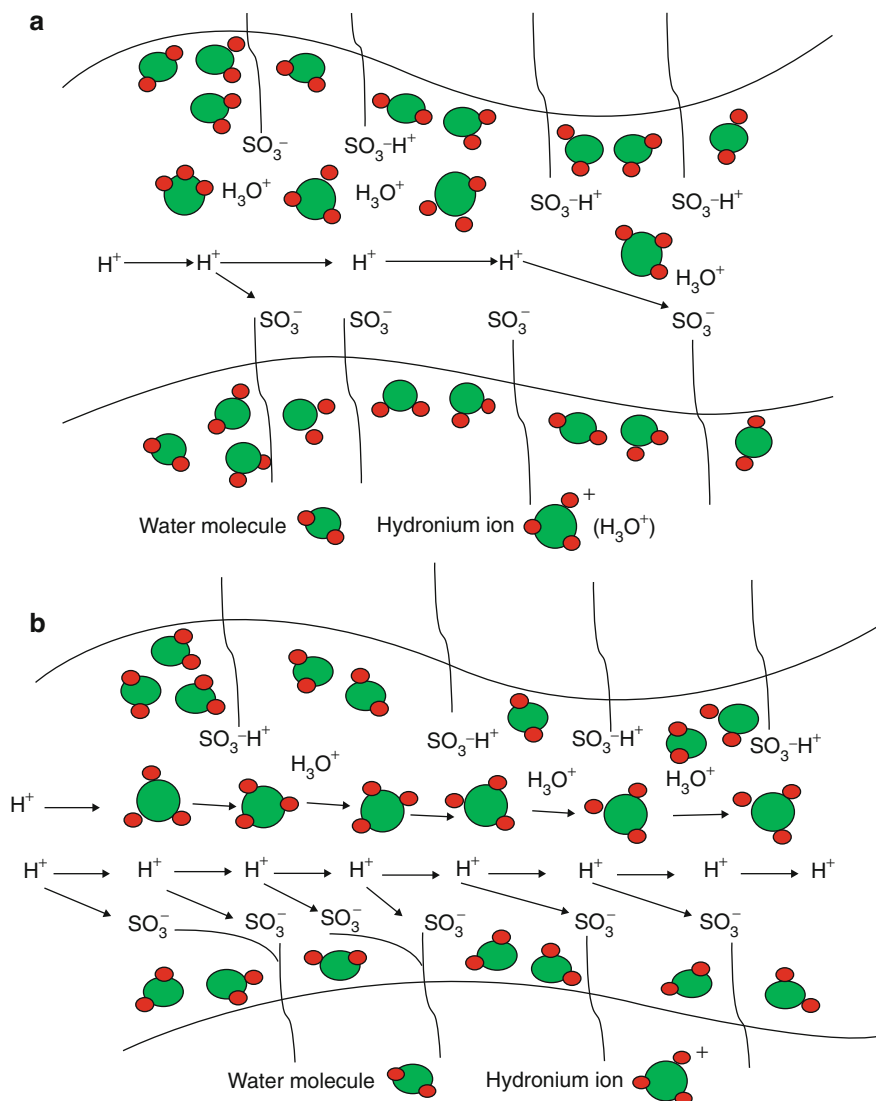


Water Competitive Diffusion, Fig. 5 Principle of fuel cell

Fuel cell (FC): Fuel cell is used for safe, pollution-free, and eco-friendly conversion of chemical energy into electrical energy through redox reaction. The membrane-based fuel cells are PEMFC and DMFC with the structure of fuel cell containing two electrodes, anode and cathode, separated by a gas-tight, proton-conducting membrane which is called as the membrane electrode assembly (MEA). The oxidation reaction that occurs in the anode produces electrons which move through the external circuit and protons that migrate from anode to cathode side through the membrane. In this process the hydration state of the membrane plays an important role as shown in Fig. 5.

At molecular level, the proton transport phenomenon occurs by two major mechanisms, i.e., jumping or Grotthuss mechanism, wherein the produced proton gets exchanged with the adjacent proton present in the sulfonic acid clusters of the solid polymer and continues until the proton reaches the cathode to complete the reaction. Thus, in the jumping mechanism the protons hop from one hydrolyzed ionic site ($\text{SO}_3^- \text{H}_3\text{O}^+$) to another across the membrane as shown in Fig. 6a.

In this mechanism, the hydrated regions are distributed randomly in the polymer matrix, which facilitates quicker transport of protons by rotation of the side chains. The ionic clusters swell in the presence of water, and proton transfer occurs through percolation mechanism. The second mechanism is vehicular mechanism, where the hydrated protons (H_3O^+) diffuse through the aqueous medium in response to the electrochemical difference and the hydronium ion ($\text{H}^+ (\text{H}_2\text{O})_x$) as a result of the electroosmotic drag carries one or more molecules of water through the membrane as shown in Fig. 6b. In DMFCs methanol permeates the membranes primarily through ionic channels, and thus the cross-sectional size of these channels influences permeability. This size is largely dependent upon the extent of membrane swelling which facilitates the permeation of both methanol and water as well as that of protons. The swelling-induced disentanglement behavior in polymer matrix is significantly responsible for the enlargement of the ionic channels and consequently for increasing methanol crossover. Hence, maintaining a high water content in the electrolyte is essential to ensure high ionic conductivity.



Water Competitive Diffusion, Fig. 6 Schematic of (a) jumping/Grotthus mechanism and (b) vehicular mechanism

Table 2 represents sorption data of fuel cell membranes. Synthetic zeolite membranes have been attractive than polymeric membranes for the recovery of polar solvents like dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAC), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), etc. They are used in different separation processes such as pervaporation, ultrafiltration, and microfiltration. The structure of zeolite is of crystalline order and, due to its narrow size pore

distribution, provides resistance toward different solvents besides stability at high temperatures.

Transport of water through the zeolite matrix comprises of three steps: (i) strong adsorption of species in the zeolite cage, (ii) surface diffusion of the species occurs from cage to cage, and (iii) vaporization of species on permeate side. In pervaporation, different mixtures such as THF/water are separated using specific types of zeolitic membranes, viz., A-type, Y-type, MOR, and ZSM-5 (Li et al. 2001). Zeolite membranes

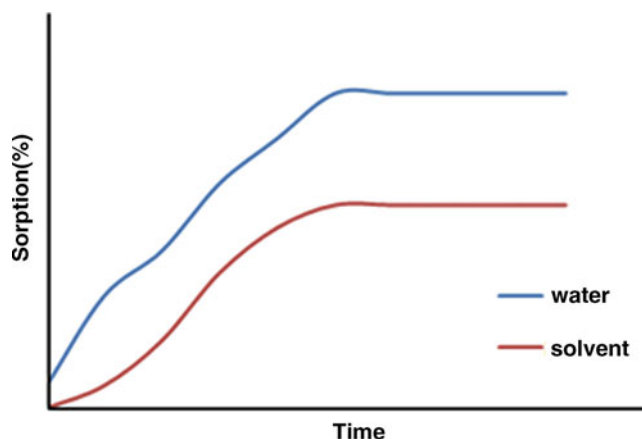
Water Competitive Diffusion, Table 2 Literature review on competitive sorption data of fuel cell membranes

S. No.	Membrane type	Water sorption (%)	Methanol sorption (%)	Methanol permeability (cm^2s^{-1})	Reference
1	CS/PVP	c	1.8	9.2×10^{-8}	Smitha et al. (2006)
2	GS-CS/PVP	52.1	0.11	7.3×10^{-8}	Smitha et al. (2006)
3	Nafion 117	33.3	9.32	21.6×10^{-8}	Smitha et al. (2006)
4	ZrSP104	56	10	69×10^{-8}	Regina et al.(2006)
5	SP57	90	70	44.6×10^{-8}	Regina et al.(2006)
6	STCF	45.6	N/A	3.71×10^{-8}	Jiang et al. (2011)
7	SPEEK	20.60	N/A	1.7×10^{-7}	Li et al. (2001)
8	SPEEK/PVDF	65	N/A	5.66×10^{-9}	Wootthikanokkhan et al. (2006)

SPEEK sulfonated polyether ether ketone, *c* highly swollen in water, not measurable, *StCF* indicating styrene and trifluoromethane sulfonic acid, *ZrSP* zirconium phosphate sulfophenylphosphonate, *CS* chitosan, *GS* glutaraldehyde, *NA* not available

Water Competitive Diffusion,

Fig. 7 Hypothetical graph between time and % sorption



are also used in catalytic membrane reactors for chemical conversion and separation within a single unit. Figure 7 shows a hypothetical curve of how competitive sorption curves appear in literature.

Cross-References

- [Membranes for Solvent Dewatering](#)
- [Water Competitive Diffusion](#)

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Water Demineralization

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Demineralization consists of removing dissolved minerals (salts, ions) from water. In fact, the large variety of existing applications for demineralized water, such as the production of potable water or its use in diverse industrial processes (e.g., electrical components production and pharmaceutical industry), among others, has particularly contributed to the actual high degree of development of membrane processes (Wang et al. 2011).

There are many demineralization technologies. They may be classified considering the main driving force used to remove ions. Membrane technologies, such as reverse osmosis (RO) and nanofiltration (NF), are those in which the main driving force is pressure; others set an electrical gradient as its driving force, such as capacitive deionization, electrodialysis, and electro-deionization, or a temperature gradient, such as distillation; and others use a chemical driving force such as ion exchange. There are also hybrid processes, mainly those including membranes to improve the efficiency of the separation process, such as thermal-membrane technologies (e.g., membrane distillation).

Proven technologies including membranes or their combination with other processes are numerous, and the mechanisms to achieve demineralization vary from each other; pressure-driven membrane demineralization technologies are mainly based on size separation, ionic charge, and diffusion, as in RO and NF. Particularly, NF is useful for reducing salt content in water, mainly of the size of bivalent ions (Ca^{2+} , Mg^{2+} , SO_4^{2-} , CO_3^{2-}), due to its 0.5–2 nm pore-size filtration range, for which a 3–20 bar pressure is necessary, but it is not able to totally reduce the mineral content. On the other hand, RO may separate

lower molecular mass compounds ($>1\text{--}0.1\text{ nm}$), mainly by diffusion, achieving the successful removal of monovalent ions (as high as a 98 % salt rejection, including Na^+ , K^+ , Cl^- , NO_3^{3-} , etc.) but increasing the required pressure for separation (5–120 bar) (Ordoñez et al. 2014; Wang et al. 2011), therefore increasing the consumption of energy as well.

The main advantages of these technologies are their technological maturity, which makes them profitable and available for numerous applications; and its total success in separating both the inorganic and organic fractions, which are not able to pass through the membranes, hence achieving not only the removal of the major part of organic and inorganic compounds in water but also disinfection, especially when a double-membrane system is used. RO process is currently the fastest growing technique for seawater and brackish water desalination, being definitely the most applied one (60 % of the world's desalination capacity), followed by distillation (34.8 %), electrodialysis (3.6 %), hybrid processes (0.8 %), electro-deionization (0.3 %), and others (0.3 %) (IDA 2011). On the other hand, preventing bio-fouling and scaling, which is directly associated with energy consumption, and the management of concentrated brines are the main challenges for these technologies to overcome.

Among electrical current-driven processes including membranes to improve demineralization, electrodialysis (ED) is the most commonly applied one. This process uses ionic exchange membranes, cationic and anionic, located in parallel separating compartments and placed between electrodes in order to separate demineralized water from concentrated water setting an electrical gradient across membrane compartments. The reverse ED process is very similar, but its cathodes and anodes can be reversed for cleaning purposes, so scaling trouble is reduced. The size of ionic solutes to be rejected or separated by ED is normally in the range of 0.00025–0.08 mm, depending on the pore size of ED membranes (Wang et al. 2011). This process cannot disinfect water as non-charged particles are not separated. Moreover, the final salt concentration is usually higher than when RO systems are applied. On the

other hand, it is a robust process that may deal with a high variety of influent water qualities. Electro-deionization is based on the same principles, but it uses ionic exchange resins to improve desalination efficiency retaining ions, therefore improving further desalination by ionic exchange membranes, thus reducing power consumption as well (Lee et al. 2013).

On the other hand, capacitive deionization is a technology that is attracting much interest, and it is currently being developed for industrial applications. It is also based on applying an electrical driving force to absorb ions onto the surface of porous electrodes that may temporarily store them, thanks to the double layer that is formed within the electrode-water interface, and the demineralized water flows into the spacer compartment. The electrodes must be regenerated when they are saturated with ions, which can be achieved by reversing polarity. This treatment may be improved by introducing ionic exchange membranes in parallel to the electrodes (membrane capacitive deionization) because they improve the retention of ions and make cleaning easier by reversing polarity (Biesheuvel and Van der Wal 2010).

Thermal treatment technologies, such as distillation, have been used to demineralize water for many years, and although distillation is the second largest technology worldwide applied for desalination, it is nowadays being replaced by RO, thanks to its versatility and lower associated costs (energy consumption, mainly). Among thermal technologies including membranes to improve separation, there are mainly two technologies that are nowadays under strong development: pervaporation and membrane distillation.

Pervaporation is a new process under development that is nowadays being introduced at an industrial scale. It is a partial pressure-driven process in which transport through the membrane is induced by the vapor pressure difference that is hold between feed and permeate vapors. Feed water is put in contact with one side of a membrane, and the permeate is removed as a low pressure vapor on the other side. This process is based on sorption and diffusion differences between water characteristics, membrane

materials, and the properties of the permeate (Baker 2004; Wang et al. 2011).

Membrane distillation combines membrane technologies with distillation processes. The water to be demineralized is first warmed up to produce a vapor that can pass through the membrane. This vapor is condensed in a cooler surface to produce the treated water, which is not able to pass across the membrane. Their main advantage is its simplicity and the low temperature gradient that is required to perform this operation. However, when the process is run applying low temperature differentials, large amounts of water must be used, which affects its overall energy efficiency. This technology is currently being under development, and different improvements are being tested, such as the use of solar energy (Ding et al. 2005).

All these technologies must deal with two main problems: fouling and scaling and the production of brines, which must be properly managed. In order to deal with fouling and scaling phenomena, feed water is usually pretreated by different technologies first, such as filtration, chemical coagulation, flocculation, or softening (Wang et al. 2011).

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Water Deoxygenation by Catalytic Membranes

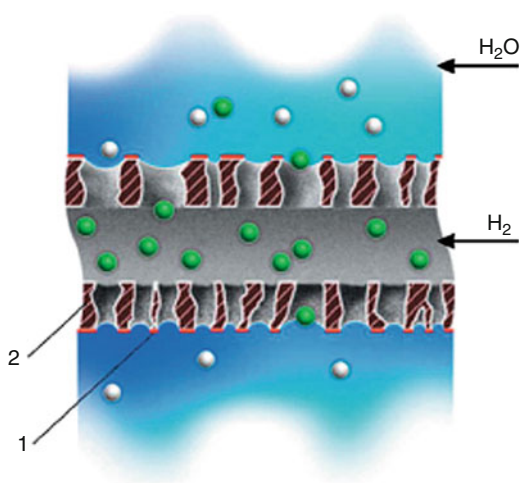
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The process of catalytic removal of dissolved oxygen (DO) from water presents an encouraging example for the industrial application of palladium catalysts supported on ion-exchange resins. Noteworthy is that the existing catalytic processes for deoxygenation of water via hydrogenation reaction involve two stages: (1) absorption of hydrogen in water and (2) passage of water containing dissolved hydrogen and DO through a fixed-bed catalytic reactor.

Catalytic membranes, i.e., palladium-loaded hollow fibers, can be prepared by deposition of palladium nanoparticles onto an outer surface of the hydrophobic porous polypropylene (PP) hollow fiber membranes and allow the DO removal from water in one stage (van der Vaart et al. 2001).

The principle of DO removal using a catalytic membrane is illustrated in Fig. 1. The hydrophobic porous catalytic membrane serves three key functions: (1) a well-defined and easily controlled location of a hydrogen–water interface, (2) accessibility of a catalyst for reagents (hydrogen and oxygen), and (3) high overall mass transfer coefficient. DO-containing water flows over the outer surface of the Pd-loaded hydrophobic hollow fiber membrane, whereas hydrogen, as a reducing agent, is supplied into the lumen side of hollow fibers and approaches the working surface of a catalyst through the pores of the membranes. Due to the catalytic activation of hydrogen adsorbed on the palladium surface, a heterogeneous reaction of DO reduction takes place. Consequently, this design allows good access of both the gas phase and liquid phase reactants to the catalyst placed on the outer membrane surface, and this system is well suited for hydrogenation reactions in aqueous media. Moreover, the reaction proceeds at room temperature. The process of water deoxygenation based on catalytic



Water Deoxygenation by Catalytic Membranes, Fig. 1 A scheme illustrating the process of DO removal from water using a Pd-loaded porous hollow fiber membrane: 1 deposited Pd, 2 polypropylene porous support (Volkov et al. 2011)

membranes is capable of achieving residual oxygen concentration below 10 ppb.

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Water Desalination in Electrodialysis Applications

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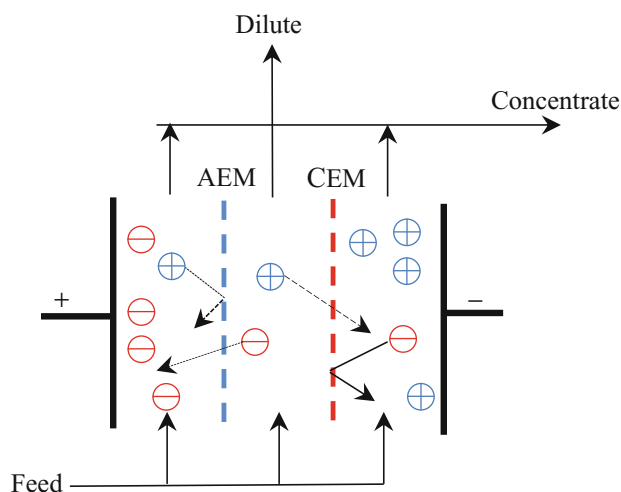
Desalination is a process that removes dissolved minerals from seawater or brackish water. About

71 % of the earth surface is covered by water which is in the form of the oceans, the seas, and the ices in the poles. However, only 2.5 % of water is fresh and suitable for drinking. Therefore, some special processes are needed to desalinate these waters. Presently, the world's total desalination capacity is around 60 million m³/day and will reach around hundred millions m³/day by 2015. 63.6 % of the total capacity is produced by membrane processes and 34.8 % by thermal processes (Drouiche et al. 2011). Among the membrane techniques, electrodialysis which is a process based on the transport of ions through selective membranes under the influence of an electrical field. Electrodialysis (ED) is an electrically driven process in which mineral salts and other species are transported through ion selective membranes from one solution into another under the driving force of direct electrical potential. Salts are in solution as ionized particles with positive and negative charges. When direct current is imposed on the solution, the positive ions migrate to the negative electrode, or cathode, and the negative ions migrate to the positive electrode, or anode (see Fig. 1) (Takashi 2007).

During the last 60 years, electrodialysis was used on a large industrial scale for the production of freshwater from brackish water. This technique is considered as reliable and inexpensive process and has proved its feasibility and high performance in the desalination of brackish water (Korngold et al. 1978). It is now well established that electrodialysis, when applied for certain range of feed water salt composition, has many advantages compared to other desalination processes (mainly reverse osmosis). In fact, electrodialysis is well suited for small to medium size plants with capacities ranging from 100 m³.d⁻¹ to 20,000 m³.d⁻¹ and feed water salinity from 1 to 5 g.L⁻¹ total dissolved solids (TDS). When the TDS exceeds 10 g.L⁻¹, reverse osmosis presents better economic advantages compared to electrodialysis. The latter, when considered for brackish water desalination, presents high water recovery rates and long membrane life and can operate at high temperature up to 50 °C. Also, the modification of the ED

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Applications,
Fig. 1 Charge transport in a conventional electrodialysis system



process in which the polarity of the applied voltage is (EDR) changed periodically, reversing the direction of ion movement. The process is known as electrodialysis reversal (EDR) and can dramatically decrease the membrane fouling or scaling. On the other hand, electrodialysis does not remove colloidal particles, matter that is not ionized and presents serious limitations when treating feed water charged with neutral toxic components such as viruses or bacteria (Strathmann 2010).

The current International Desalting Association World Desalting Plants Inventory shows that 13.7 % of the brackish water desalting capacity in the world is ED and EDR.

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Water Disinfection by Membrane Operations

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Nowadays, more and more drinking water are produced by membrane technology, especially from fresh water using microfiltration or ultrafiltration. That can be explained by the fact that ultrafiltration membranes exhibit a high or even complete level of viruses, bacteria, and protozoa cysts (*Giardia* and *Cryptosporidium*) removal.

However, membranes and membrane modules can be damaged during water production, causing a loss of membrane system integrity and leading to the passage of pathogens through membranes and the contamination of filtered water. Thus, accurate and efficient integrity tests of membrane systems are necessary to guarantee the quality of filtered water. That is why a lot a research were carried out to develop the best membrane integrity test. Among them, direct and indirect membrane integrity tests can be distinguished.

Direct membrane integrity tests are directly applied to membranes or membrane modules. In this category, pressure decay test (PDT) and

diffusive air flow (DAF) test can be cited (Adham et al. 1995; Johnson 1998). Such tests characterize directly membranes or membrane modules structure to evaluate the pathogens removal, but they are conducted off-line. Indirect membrane integrity tests characterize filtered water quality parameters to evaluate the ability of membranes or membrane modules to remove pathogens. Particle counting (Panglisch et al. 1998) and turbidity monitoring (Banerjee et al. 2001) are indirect membrane integrity tests. They can be conducted on-line, but they are not able to detect water quality changes at the levels required to ensure pathogen removal. Among these tests, PDT and DAF test are the most frequently used tests in drinking water production due to their advantages of simplicity, low maintenance, reliability, and high sensitivity to detect membrane breaches.

Among the last developments in membrane integrity field, except Phattaranawik et al. (2008) who proposed a new membrane integrity test based on monitoring relative transmembrane pressure created by two intact membranes in series, all the other developments were focused on the characterization of filtered water quality: microbial challenge test (Brehant et al. 2010), nanoscale probe challenge test (Gitis et al. 2006), and magnetic nanoparticle challenge test (Guo et al. 2011).

The sensitivity of the membrane integrity test is an important factor to be considered. This parameter is a relevant indicator to guarantee the pathogen removal credit. Generally, the sensitivity of membrane integrity tests is expressed in terms of log removal value (LRV) of pathogens in drinking water. PDT and DAF test are able to detect membrane integrity at high levels of 5–6 LRV, even more than 6 LRV for DAF test.

The frequency of the membrane integrity test is important in order to maintain specific LRV requirements. There are no common guidelines for the frequency of membrane integrity tests. Membrane integrity test frequency needs to be related to a risk assessment as the first priority and operational practicality as the second priority. In the case of hollow fiber membranes, the frequency of membrane integrity test can be calculated, given an expected number of fiber breaks per year and a LRV target (Bennett 2005).

Today, the perfect integrity test has not been found. Thus, it remains essential to develop an alternative on-line monitoring test to better satisfy regulatory requirements for drinking water industry. This “ideal” test should be quick, sensitive, accurate, simple, continuous, and relatively inexpensive to be developed at industrial scale.

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Water Electrooxidation

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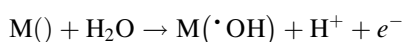
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By using a high O₂ evolution overpotential anode, water electrooxidation can be considered as an indirect anodic oxidation process. It can be

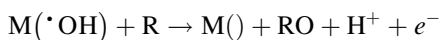
classified as an electrochemical advanced oxidation process (EAOP) because it leads to the in situ production of the hydroxyl radical ($\cdot\text{OH}$), the second powerful oxidant (after fluorine) with $E^0(\cdot\text{OH}/\text{OH}^-) = 2.80\text{V}/\text{SHE}$. Hydroxyl radical is a very reactive species (Brillas et al. 2009; Oturan and Aaron 2014) able to mineralize any organic pollutant. Therefore, this indirect anodic oxidation process is used in order for destruction of bio-refractory pollutants.

In this process (Panizza and Cerisola 2009), $\cdot\text{OH}$ s are produced at anode surface from water oxidation using a high O_2 evolution overpotential anode such as boron-doped diamond (BDD) electrode, from the following electrochemical reaction:

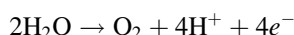


where M represents the anode material and $\text{M}(\cdot\text{OH})$ hydroxyl radical adsorbed on the anode.

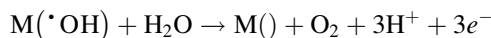
Pollutants (R) are then oxidized as follows:



Under polarization, an undesirable reaction is water oxidation to dioxygen (called oxygen evolution reaction):



When oxygen evolution reaction is concomitant with hydroxyl radical formation, it leads to radical desorption:



The rate of this secondary reaction depends on the anode material and the applied potential. Table 1 gives the potential for oxygen evolution reaction (OER) on different anodes in different conditions.

It can be then distinguished as anodes with good catalytic properties for OER (i.e., low oxygen evolution overpotential, DSA (dimensionally stable anode), RuO_2 , IrO_2 , Pt, and graphite) to anodes with poor catalytic properties for OER (i.e., high oxygen evolution overpotential, SnO_2 , PbO_2 , and BDD). Those two types of anode are

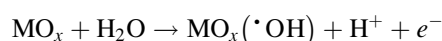
Water Electrooxidation, Table 1 Potential for oxygen evolution reaction (OER) on different anodes in H_2SO_4 . Standard potential for OER is 1.23 V versus SHE

Anode	Value versus SHE	Conditions
RuO_2	1.47	0.5 M H_2SO_4
IrO_2	1.52	0.5 M H_2SO_4
Pt	1.6	0.5 M H_2SO_4
OPG ^a	1.7	0.5 M H_2SO_4
SnO_2	1.9	0.05 M H_2SO_4
PbO_2	1.9	1 M H_2SO_4
BDD	2.3	0.5 M H_2SO_4

^aOPG oriented pyrolytic graphite

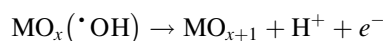
currently proposed (Comninellis 1994) to describe indirect anodic oxidation and called “active” and “nonactive” anodes.

Whatever is the type of anode (schematized MO_x), the first step of the process is the oxygen transfer reaction (discharge of water molecule) to form adsorbed hydroxyl radicals:

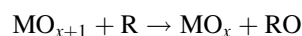


The following steps can be distinguished for “active” and “nonactive” anodes.

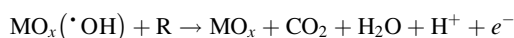
At “active” electrodes, higher oxidation states of the material are possible, and then, the production and adsorption of $\cdot\text{OH}$ form a higher oxide:



A redox couple $\text{MO}_{x+1}/\text{MO}_x$ called “chemisorbed active oxygen” is then formed at the electrode surface and can be engaged in a selective and partial oxidation of the pollutant R:



At “nonactive” electrodes, hydroxyl radicals are physisorbed as “active oxygen” because of the stability of the electrode surface and can act for the nonselective and total oxidation of the pollutant R to CO_2 :



Hence, it is possible to combine indirect anodic oxidation at the anode with the electro-Fenton

process in bulk (by using a carbonaceous cathode) to get a high mineralization rate of pollutants. In this case, $\cdot\text{OH}$ is formed simultaneously at the anode as well as in the bulk solution from the electro-Fenton reaction at the cathode; the oxidation power and mineralization efficiency of persistent organic pollutants are then extremely high (Dirany et al. 2010).

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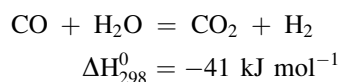
Water Gas Shift (WGS)

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In the last decades, great attention has been paid to hydrogen as a carrier to be used for the production of clean energy by means of new technologies, designed to enhance efficiency and environmental sustainability, especially for power generation. Hydrogen is also utilized in a large amount in the chemical and petrochemical industry for ammonia synthesis, hydrocracking, hydrotreating, etc. Currently, hydrogen is mainly produced from fossil fuels (96 %): the stream coming out from a reformer or a coal gasification plant contains about 50 % H_2 that

has to be recovered and 40–45 % CO which can be utilized for producing more hydrogen. Thus, an upgrading stage is required, and the water gas shift (WGS) reaction is the most feasible one for this purpose. The water gas shift reaction is



Low temperatures thermodynamically favors CO conversion, but pressure (in a traditional reactor) does not affect it since the reaction is exothermic and characterized by no variation of the mole number.

Kinetics is promoted by a high temperature and slightly depends on the feed pressure.

WGS process is conventionally operated in two fixed-bed adiabatic reactors, in series, with a cooler interposed between them. So the WGS traditional process consists of:

1. A first reactor operating at high temperatures (300–450 °C) and GHSV (20,000 h^{-1} , gas hourly space velocity), using $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst (Bustamante et al. 2004; Keiski et al. 1996; Ullman's Encyclopedia of Industrial Chemistry & 5th Completely Revised Edition 1995) which shows high kinetic activity when operated at a temperature higher than 300 °C. Taking advantage of the high reaction rate, this reactor converts the most of CO .
2. A heat exchanger for cooling the stream from 400–450 °C down to 200 °C ca.
3. A second reactor operating at lower temperatures (210–300 °C) and GHSV (2,000 h^{-1}) for reducing the CO fraction in the gaseous stream to less than 1 %. This reactor uses CuO-ZnO - (Bustamante et al. 2004; Ullmann's Encyclopedia of Industrial Chemistry & 5th Completely Revised Edition 1995; Amadeo and Laborde 1995) or CuO-CeO_2 -based catalysts and takes advantage of the low temperatures displacing the equilibrium, since the exothermic character of the WGS reaction.

$\text{H}_2\text{O}/\text{CO}$ feed molar ratio typically ranges from 2 to 5 for shifting the thermodynamic equilibrium

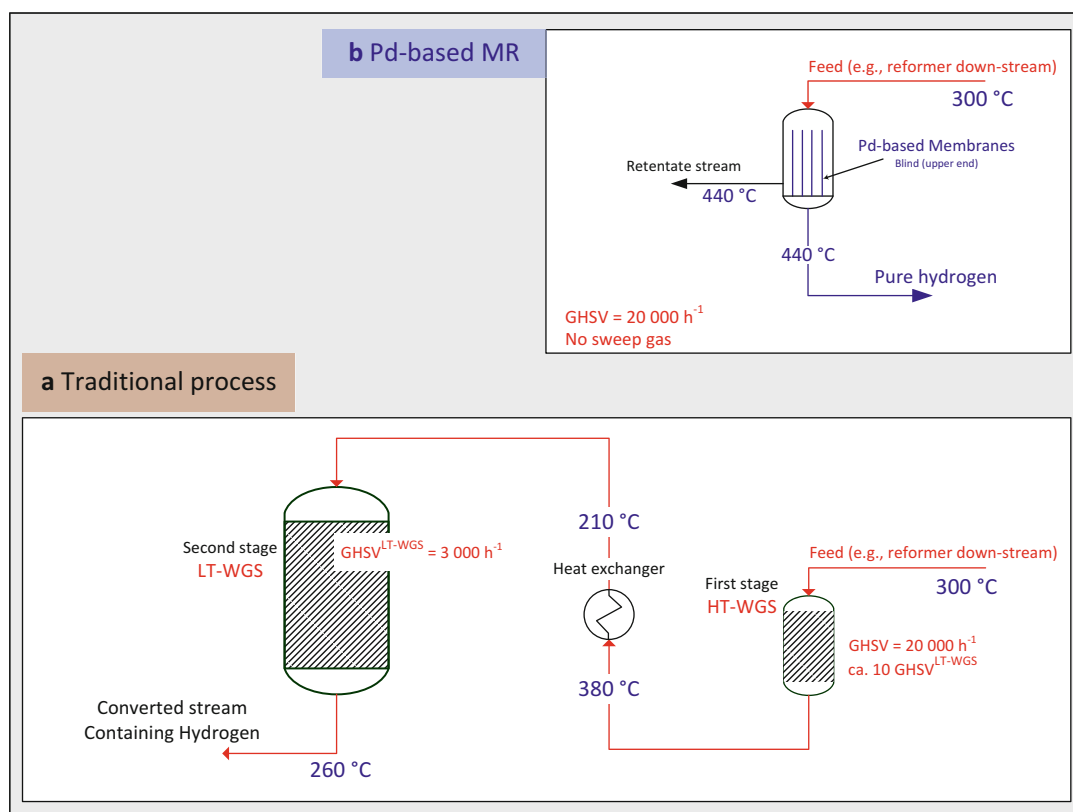
conversion and increases the reaction rate and thus hydrogen yield. The WGS is often followed by a further step of remaining CO elimination since CO is a poison for many industrial catalysts. Thus, this H₂-rich stream is usually directed to a CO selective/preferential oxidation reactor and then to a pressure swing adsorption unit for separating H₂ from the other gases.

For providing a better exploitation of raw materials together with the reduction of the reaction/separation/purification stages and related loads, the use of membrane reactors (MRs) is a promising approach, as they combine the reaction and the H₂ separation by means of a selective membrane (Brunetti et al. 2012a; Shu et al. 1991; Uemiya et al. 1991; Dittmeyer et al. 2001; Brunetti et al. 2012b).

The presence of the membrane allows the recovery of a hydrogen-rich/pure stream which

does not require any additional separation. Moreover, the removal of the hydrogen, which is a product, from the reaction volume shifts the reaction toward a further conversion.

The removal of hydrogen by a membrane gives many advantages: the reverse reaction rate is depleted owing to the lower H₂ concentration; the residence time of reactants is increased; the thermodynamic equilibrium of a membrane reactor exceeds that of a traditional reactor; the pressure has a positive effect on conversion in a membrane reactor, even if no variation in the number of mole is involved in the WGS reaction (Marigliano et al. 2003). Therefore, the use of a membrane reactor allows obtaining a higher conversion also at higher temperature where the thermodynamic conversion is low, acting positively on the kinetics. Consequently, the amount of catalyst necessary for a given conversion can be



Water Gas Shift (WGS), Fig. 1 Schemes of “Pd-based membrane reactor” and “traditional process” for WGS reaction (Marigliano et al. 2003)

significantly reduced (Barbieri et al. 2011). In fact, one membrane reactor operating at high temperature was demonstrated replacing the two reactors of the traditional process (Fig. 1), giving the same final conversion or higher.

Among the several membrane types, the Pd-alloy membranes are the most used for the selective removal of hydrogen in applications such as dehydrogenation reactions, thanks to their infinite H₂ selectivity. An important aspect in the use of Pd-alloy MR is the good exploitation of whole the available membrane area, which allows the improvement of the global performance, with higher CO conversion and more H₂ recovered in the permeate side (Barbieri et al. 2008).

Currently, self-supported Pd-Ag membranes are produced at commercial level, and, when used to investigate experimentally the WGS reaction at a laboratory scale, they showed a high durability and performance stability for more than 2 years operating at 330 °C and up to 10 bar (Barbieri et al. 2008).

The results obtained at a laboratory scale concretized in some cases in various patents. For example, United Technologies Corp. patented the use of a WGS MR, comprising a WGS reaction region a permeate volume, separated by an H₂-separation membrane which allows H₂ formed over a catalyst in the reaction region to be passed selectively to the permeate region (Gummalla et al. 2010).

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Water Purification

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Water purification refers to the production of potable water from a variety of sources, including groundwater; surface sources like lakes, rivers, sea, or brackish water; artificial reservoirs; and sewage treatment plants. The first three sources are linked together in the so-called water cycle, where moisture present in the atmosphere

condenses, generating precipitation; in turn, this reaches the ground, vegetation, and other surfaces. Part of this water evaporates back in the atmosphere, while another fraction infiltrates the ground, replenishing groundwater reservoirs as well as supplying natural (and artificial) water bodies. Human activity interferes with this natural cycle abstracting water from ground and surface sources and adding pollutants, solids, and contaminants to it. Modern water management includes treating waste streams produced by human activity as well as producing potable water from saline sources and creating artificial surface reservoirs.

Rainwater is not pure but contains dissolved gases, particulate, and bacteria picked up during its fall. Therefore, it is not pure water but it is very *soft*. Surface water, washing over soil and other surfaces, carries with it any mobile or dissolvable substance, including bacteria, soil, and vegetation. Water percolating in the ground and accumulating in groundwater reserves dissolves mineral along the way and is usually classified as *hard* water, depending on the composition of the soil through which it has percolated. Municipal, agricultural, and industrial wastewater streams all have specific contents, for example, high nitrate content in agricultural or high sulfur content in industrial waste.

Water purification is distinct from the more general water treatment entry as the latter covers a more diverse range of waters sources, e.g., agricultural and industrial waste streams or soil decontamination.

Water purification to make water potable is typically performed in treatment plants, but treatment at the point of origin, whether a well or a reservoir, can be the preferred option. Examples include altering the pH of raw water in a well as this could damage piping and pumps from well to plant or controlling aquatic life in a lake after the introduction of foreign species has altered its ecosystem (e.g., zebra mussels in the Great Lakes region in North America), leading to overgrowth of plant life or low oxygen levels. The different nature of water sources requires distinct purification methods to achieve potable water requirements, which are set country by country and are based on the maximum acceptable concentration

of dissolved gases, minerals, solid, and microorganisms that can be found in potable water (Nemerow et al. 2009). Regardless of these differences, the main steps in water purification are similar in water treatment plants around the world. First, sampling is performed at every stage of the treatment process to evaluate quantitatively water quality and to monitor each step's effectiveness. Common quality controls include turbidity, testing for taste and odors, pH, alkalinity, solid residue, or bacteria concentration. For a more extensive treatment of water quality analysis, the reader is referred to the further reading section at the end of this text. Pretreatment processes include screening and sedimentation to remove solids, plants, or other floating debris that could damage the plants' equipment (Pizzi 2010). Smaller particles that will not settle in a reasonable time or can pass screens are traditionally removed using coagulation or flocculation. These particles will resist settling due to their small size (which increase drag resistance) and their surface charge that repels particles one from the other. Coagulation and flocculation act by neutralizing the particles' surface charge, thereby inducing their aggregation in bulkier structures (called flocs) that eventually grow large enough to settle. In modern plants, this stage is more and more replaced by membrane filtration or a combination of coagulation and filtration. The advantage is a significant reduction in process time as well as minor use of chemicals (Koltuniewicz and Drioli 2008). A further sedimentation step, also called clarification, is sometimes added after flocculation to remove large amounts of chemical precipitates resulting from water softening. The latter can also be effectively achieved using nanofiltration membranes (Koltuniewicz and Drioli 2008). Precipitates, flocs from coagulation or flocculation, and microorganisms are removed from water during the filtration process, whereby water passes through filter media (sand, granular activated carbon, garnet, or anthracite) leaving behind the solids. A primary task of the filtration stage is to reduce the water's turbidity, not only for aesthetic reason but also because it interferes with light-activated disinfection (Parker et al. 2009). For further

details on filtration, the reader is referred to the further reading section at the end of this text. Membrane bioreactors, which combine a biological reactor to degrade suspended organic matter with a membrane for solid/liquid separation, are becoming an increasingly popular alternative to the above purification steps due to a reduced footprint and higher-quality output (Judd 2011). The following step in the purification process is water disinfection, where pathogen organisms, such as viruses, bacteria, or fungi, which can cause diseases, are destroyed or removed. Common water-borne diseases caused by incomplete disinfection include hepatitis, caused by a virus; legionellosis, caused by bacteria; or dysentery, caused by protozoa. Disinfection should not be confused with sterilization, which entails the destruction or removal of all microorganisms from water and is required only for specific uses (e.g., high purity water for industrial use). Disinfection can be achieved using heat, UV light, or chemicals. The first, essentially boiling water, is today used only in emergencies or when no other treatment method is available. UV treatment is very effective at removing most pathogens, including the dangerous and hard to remove cryptosporidium. For it to be effective, turbidity has to be low enough not to block the light. Furthermore, natural organic matter and dissolved minerals have also to be removed to prevent fouling of the lamps. UV treatment alone is not sufficient to ensure complete disinfection and is often used in conjunction with chemical treatment, sometimes as a polishing step after the latter.

Chemical treatment is by far the most common disinfection method, with chlorination being the primary process. Chlorine is available in gaseous, liquid, or solid forms and reacts with the different substances present in the water to form either active or inert residuals. Precise guidelines control the choice of chlorine source and its dosing. Other chemical used in disinfection include bromine, which is less stable than chlorine; iodine, which can be easily transported in solid form; ozone, which produces less toxic residuals than chlorine; and potassium permanganate, which is often added to water before chlorine to eliminate humic and fulvic acids, which, upon chlorination,

produce trihalomethane, a toxic substance. Nanofiltration and reverse osmosis membranes have been shown to be effective alternatives, completely removing virus and bacteria (Koltuniewicz and Drioli 2008), though in general are not yet competitive with chemical treatment. For further details on filtration, the reader is referred to the further reading section at the end of this text.

Other water purification processes can include fluoridation, which is applied to achieve an optimal concentration of fluoride ion in water, to provide public health protection from dental caries; remineralization, when reverse osmosis is used during the filtration process as it removes all dissolved ions from the treated water; softening to remove carbonates, sulfates, and nitrates found in groundwater; and anticorrosion and anti-scaling processes which are meant to protect plant equipment and piping from chemical or organic attack.

Emerging Challenges in Water Purification

Micropollutants are compounds found at the ppm- or ppb-level concentration in water and soil that are considered as potentially harmful to the environment and human health. These include different classes of compounds, from pesticides to pharmaceutical active compounds and hormones, surfactants, and person care products (Stuart et al. 2011). For most compounds, there is yet little evidence of the effects of long-term exposure or of slow accumulation in the environment and in human food supply chain (Deblonde et al. 2011). Nonetheless as these results are made available in the scientific literature, it is expected that legislation in developed countries will require their removal from drinking water (Shannon et al. 2008). This will require, most likely, novel detection and removal methodologies for micropollutants, given their very low concentration (Virkutyte et al. 2010).

Nanomaterials, whose characteristic is to have at least one dimension less than 100 nm (10^{-7} m), are a novel class of potentially harmful materials, for which detection and removal strategies from

wastewater are only now being developed (Nowack and Bucheli 2007). At the same time, nanomaterials are also being intensively being investigated to improve removal of contaminants and decrease the energy consumption of wastewater treatment processes (Qu et al. 2012). As the effects of long-term exposure to nanomaterials are not yet known, water regulators and health agencies around the world have adopted a cautious approach, banning or severely limiting the use of nanomaterials in wastewater treatment and water purification (Ganzleben and Hanen 2012).

Cross-References

► [Nanofiltration](#)

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Water Recovery in Paper Industry by Membrane Operations

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Papermaking consumes high volumes of water. In a modern paper mill, the water consumption can be less than 10 m³ water per 1 ton of produced paper, but in older mills the water consumption can be significantly higher. The use of membrane processes enables the reduction of water consumption to values below 10 m³ per 1 ton of produced paper.

In efforts to decrease the water consumption of paper mills, the greatest benefits can be achieved by treating and recycling the effluent streams with greatest volumes. For instance, ultrafiltration of paper machine clear filtrate (a paper machine white water), which can constitute more than half of the total effluent load of a paper mill, enables significant reduction in freshwater use. Ultrafiltration removes from the clear filtrate suspended solids and microorganisms and reduces the amount of organic dissolved compounds (lignin, hemicellulose, etc.). Ions are retained when they are bound, for example, to fibers. The removal of dissolved organic compounds depends on the quality of the clear filtrate and the used membrane, but it is typically between 10 % and 40 %. The clear filtrate purified with ultrafiltration can be used at wire section showers, as sealing water and in dilution of wet-end chemicals. Nanofiltration removes, depending on the clear filtrate, filtration conditions and the used membrane from 70 % to 90 % of dissolved organic compounds (COD, TOC), color, and lignin degradation products. In addition, nanofiltration can retain multivalent ions.

For instance, at SAPPI Ltd Kirkniemi paper mill (Lohja Finland), the use of membrane filtration in recovery of water has made it possible to decrease the freshwater intake to values below 6 m³ per produced ton of paper. At Kirkniemi paper mill, high shear rate cross-rotational

(CR) filters (Valmet Corp.) are used in the ultrafiltration. The membrane area is 1,428 m². When the membrane plant is operated in three stages, 94 % of the clear filtrate (feed) can be recovered into permeate (235 m³/h). In a 7-year period, a very high average flux, 315 L/(m²h) (0.8 bar, 60 °C), has been reported. The produced permeate is used at paper machine showers and for chemical dilutions. A part of the permeate (50 m³/h) from the ultrafiltration is possible to purify further with spiral-wound nanofiltration to replace warm freshwater of the paper machine (Sutela 2008).

The CR filtration technology (Valmet Corp.) has been applied also in the treatment of paper mill waters at the newsprint mill of Holmen Paper in Madrid (Spain) and UPM Kymmene mill in Valkeakoski (Finland). At these mills, approximately 20–50 % reduction in the use of freshwater has been achieved (Sutela 2008). Also vibratory shear-enhanced processing (VSEP) filters, tubular modules, and conventional spiral-wound modules have been used in several mills in purification of paper mill circulation waters (Linpac 2006; Kreutzman and Sutela 2004).

Water is recovered with membranes also from the effluents of the external biological treatment plant of paper mills. For instance, in the Eltmann newsprint mill of Papierfabrik Palm (Germany), nanofiltration has been used since 1999 to purify the effluent and recover water back to the paper-making process. The produced concentrate is first precipitated by lime to remove the compounds, which are difficult to degrade biologically, and then the concentrate is led back to the biological purification process (Schirm et al. 2001). Also membrane bioreactors (MBR) are used in recovery of water at paper mills. One reported example operates in France at the Papeteries du Rhin's paper roll mill, where MBR purifies the mill effluent, and permeate of the process is partly led back to the mill processes (Ramaekers et al. 2001).

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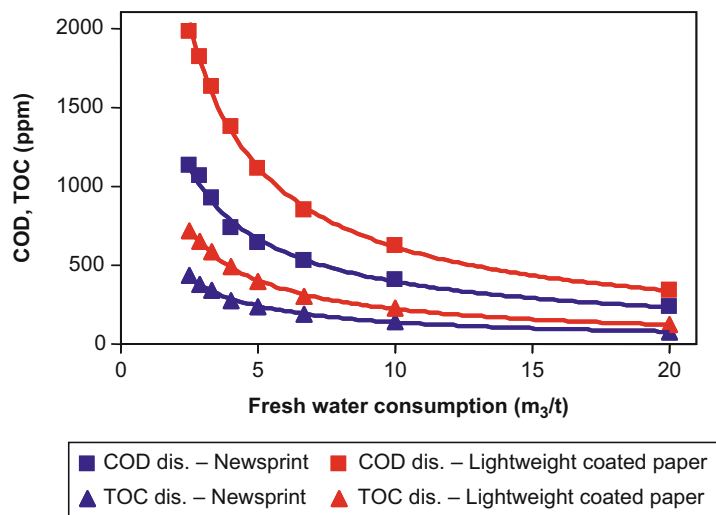
Water Recovery in the Paper Industry, Membranes for

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There exists a worldwide trend in paper industries to reduce freshwater consumption for environmental and economic reasons (water stress, freshwater savings, and reduction of effluent treatment and disposal costs). In modern paper mills, freshwater consumption can vary between 2 m³ and 20 m³ of water per ton of paper produced, depending on the type of manufactured paper

Water Recovery in the Paper Industry, Membranes for,

Fig. 1 Accumulation of dissolved COD and TOC in recycling paper mill using newsprint and lightweight coated paper as raw material (Miranda et al. 2009)



and on the age of the mill. As the mills increase the closure of their water systems, a considerable accumulation of contaminants exists; this is worse in recycling paper mills. Accumulation of contaminants, as shown in Fig. 1, can affect both product quality and efficiency of the papermaking operations. Therefore, an adequate internal purification of the process waters is necessary to reduce the organic and inorganic load of the water before its recirculation.

Various internal purification techniques are used nowadays to remove the contaminants from the process waters, including membrane-based processes (Nuortila-Jokinen 2003; Monte et al. 2011). For an advanced white water treatment (water removed from the web in the paper machine), complete elimination of suspended solids is necessary, while for the internal treatment of other process waters the elimination of dissolved substances is also required.

Membrane-based processes are able to produce water with different qualities according to the needs of the process. Moreover, the energy consumption of membrane filtration may be economically viable and the modern modules may be fit in existing mills. Furthermore, they may be installed close to the point in which water must be treated. Ultrafiltration is considered as a best available technology in the BREF Integrated Pollution Prevention and Control (2015) to treat the clear filtrate produced in paper mills during the

purification of white water by disk filters. The clear filtrate can constitute more than half of the total effluent load of the mill. Thus, recycling the purified clear filtrate back to the papermaking process significantly reduces the total effluent load. However, clear filtrate must be filtrated by adequate membranes to obtain a high quality permeate which can be reused, for instance as wire section shower water and in the dilution of chemicals, reducing freshwater consumption (Nuortila-Jokinen et al. 2004; Judd and Jefferson 2005; Kallioinen et al. 2010). The improvements of membrane filtration and the development of low fouling membrane processes have made that this technology is now widely used in the paper sector although fouling and erosion of the active layer still remain as critical factors for its further implementation.

The main requirement for a membrane used in the treatment of clear filtrate or process water in papermaking is a high and stable capacity because of the huge volumes of the pulp and paper mill process streams. The main factor causing flux decline and operational breaks in a membrane filtration process is fouling. It originates from the combined effects of different factors on the membrane: process conditions, process water content, and membrane characteristics. The easiest way to optimize the filtration process to ensure a low fouling process is to choose an optimal membrane for filtration, because it is not possible to change

the process conditions or the process water composition (Duranceau 2001).

Membrane fouling can be reduced by using the shear enhanced membrane modules, adjusting the operating parameters, taking into account the interactions between the membranes and the solutes, and applying different pretreatment to the feed stream (Nuortila-Jokinen 2003). Conventional pretreatment strategies, before membrane filtration, include chemical coagulation, adsorption, sedimentation, and flotation. For example, by causing suspended materials to be agglomerated into larger-size units, coagulation can serve as a kind of pretreatment for kidney operations, having the potential to increase throughput and reduce the rate of blockage of pores in an ultrafiltration membrane.

Membrane Material and Cut-Off

Membrane material is being turned out to be more hydrophilic and more or less negatively charged as paper mill wastewaters are mainly contaminated by negatively charged substances, and this creates electrostatic repulsion forces between the membrane and the solutes decreasing permeability and increasing fouling. Regenerated cellulose membrane has been found to be an optimal and stable membrane in operation for purification of paper mill process water, owing to its remarkable hydrophilic properties. Regenerated cellulose is a pure cellulose which has been treated in a chemical bath for better chemical resistance. However, they do not have good performance stability at high temperature. In paper mills, membranes should also be able to perform at temperatures above 60 °C, because the temperature of the process waters increases as the mill water circuits are getting closed. Membranes which have a better thermal and chemical resistance than the regenerated cellulose might be competitive, for instance, polyethersulfone or hydrophilic polysulfone, polypropylene (Cheryan 1998; Duranceau 2001; Puro et al. 2010). Hydrophilic polysulfone has showed better performance to fouling in a recycled paper mill.

On the other hand, under hydrostatic pressure a polymeric porous membrane is compacted leading to a denser membrane structure with smaller pores and lower membrane flux (Kallioinen et al. 2007). In addition to the influence on flux, membrane compaction can affect retention. If the membrane compaction causes a decrease of the membrane pore size or a deformation of the pore geometry, the retention of molecules of the same magnitude as the membrane cut-off value or of smaller molecules than the cut-off value might increase.

Membrane Module Structure

Several modules are used in the paper industries (Table 1). The differences between the traditional modules and the shear enhanced modules are related to the flux and the fouling of the membranes. In the shear enhanced modules, the turbulence created by different systems close to the membrane surface decreases the fouling and, therefore, increases the flux through the membrane. For this reason, the vibration shear enhanced processing and cross rotational filter modules are preferred in internal purification treatments for process water in papermaking, although their application must be evaluated because the vibration and shear may erode the membrane active layer.

Module Operation Parameters

In general, the lower the pressure and the higher the shear on the membrane surface, the higher the flux and the less fouling occurs but membrane erosion may occur.

Papermaking Process Conditions (pH, Chemical Composition, etc.)

The flux is also greatly influenced by the feed pH. Lower fluxes are obtained at acid pH, but it is not always possible to change the conditions of the process. Sudden changes in the pH or

Water Recovery in the Paper Industry, Membranes for, Table 1 Advantages and disadvantages of the membrane module structure

	Modules	Advantages	Disadvantages
Traditional modules	Tubular	Tolerate high concentrations of suspended solids	Low fluxes Poor packing density Very large plants
	Plate and frame	Better packing density	Low fluxes Very easy to plug with suspended solids (fouling)
	Spiral wound	Relatively low price	Low fluxes Very easy to plug with suspended solids (fouling) Pretreatment must be used
	Hollow fiber	Best packing density	Low fluxes Very easy to plug with suspended solids (fouling)
Shear enhanced modules	Vibration shear enhanced processing	High fluxes Reduced fouling	—
	Cross rotational filter		—
	Tubular compact module		—

temperature may set their own demands for the membrane process. Therefore, the membrane should be selected taking into account the extreme conditions that could happen in the process.

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Water Recycling in Electroless Plating by Membrane Operations

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Electroplating or metal finishing processes are characterized as water-intensive operations that are associated to a large liquid effluent volume, and by consequence it generates a large volume of

contaminated wastewater. Electroless metal plating is a chemical reduction process that provides a uniform plating thickness on the metal surface plating part. It is a non-galvanic plating method that involves several simultaneous reactions in an ► [aqueous solution](#), which occur without the use of external electrical power. The reaction is accomplished when hydrogen is released by a reducing agent, normally sodium hypophosphite, and oxidized, thus producing a negative charge on the surface of the part. The most common electroless plating method is electroless nickel plating, although silver, gold, and copper layers can also be applied in this manner. The solvent cleaning is the first cleaning step in the plating process using an organic solvent to remove oil-grease from the surface of work pieces. The latter requires high purity rinse water (10–15 M Ω .cm) to avoid any blemishing or deterioration of the plated metal (Wong et al. 2002). Rinsing waters become contaminated during the plating process due to “drag-out” from the previous plating baths. The contaminated rinse waters may contain heavy metals such as chromium, copper, zinc, lead, nickel, and iron, as well as monovalent ions, depending on the plating process and emulsified organic solvent and oil-grease.

Plating wastewater is usually treated with physical and chemical method (conventional techniques), or most commonly followed by biochemical ways such as the activated sludge method, but the treated wastewater is still highly saline and cannot be reused or rejected in the wastewater discharge network. Therefore, in order to produce qualified water that can be recycled in production line, traditional wastewater plant needs more advanced and efficient treatments such as electrolytic reclamation, ion exchange, reverse osmosis, or electrodialysis.

These methods are used not only to solve the problem of heavy metal pollution but should also deal with the loss of the usable metal in the electroplating industry, which is becoming increasingly expensive due to a decrease in the quality of metal ores. In fact, what is needed is an economical method, not only for the removal of

heavy metals from wastewater but also for the recovery of these metals (Benvenuti et al. 2014).

Membrane separation has become increasingly attractive for treatment and recycling of wastewater in mechanical industry as it is highly efficient, easy to operate, and of low cost. However, treatment of wastewater containing organic solvent using a membrane process posed a considerable challenge, as few polymeric membranes can tolerate a wide range of organic solvents. Recently, reuse of spent rinse water from metal plating using reverse osmosis has been studied. High-quality effluent with 45 μ S/cm conductivity was obtained. Integrated membrane process of ultrafiltration/reverse osmosis (UF/RO) for the reclamation of spent rinse water from an electroless plating process can be considered. Ultrafiltration can be both considered for the pretreatment prior to reverse osmosis and for emulsified oil/water separation. Nanofiltration (NF) membranes have properties in between those of ultrafiltration (UF) membranes and reverse osmosis (RO) ones. The significance of this membrane, besides having small pores, is the membrane's surface charges, which allows charged solutes that are smaller than the membrane pores to be rejected along with bigger neutral solutes and salts. Furthermore it is capable of rejecting multivalent ions effectively, and on the other hand lets the monovalent ions pass through. These are the characteristics that make the nanofiltration membrane a potential process to reject heavy metal ions, which in general are multivalent ions. A complex system comprised of microfiltration, UV radiation, carbon adsorption, nanofiltration, and ion exchange was applied for recycling of spent final rinse of an electroless plating operation.

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Water Reuse

► [Membrane Bioreactor for Decentralized Wastewater Treatment: A Case Study](#)

Water Reuse and Recycling in Pulping Plants by Membrane Operations

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Pulp production is a water-intensive process. A conventional kraft pulp mill can use up to 40 m³ of fresh water to produce one ton of chemical pulp (Reeve and Silva 2000). The tightening legislation aiming to the protection of environment and the growing lack of pure water resources leading perhaps to limitations in water use at the mills are driving forces to decrease water consumption also at pulp mills. In the future the cost of water might also be higher due to the lack of resources.

There are real-life examples, where membrane technology has already been used in the decrease of freshwater consumption of pulp mills. For instance, at the VHP security paper mill owned by Ugchelen BV (Apeldoorn, Netherlands), a wastewater purification process has been developed, in which dissolved carbon dioxide is used in a flotation process to remove fibers and debris and simultaneously to reduce the effluent pH from 11 to 8.2 prior to a membrane bioreactor (MBR) unit. The MBR operates at thermophilic conditions in order to reduce the need for heating the purified water. A tubular PVDF membrane is installed outside the bioreactor (volume 250 m³). The COD of the influent of the MBR is 3500 mg/L and the COD of the effluent are stabilized to about 500 mg/L. The effluent is recirculated to the mill processes without any detrimental effect in the product quality. The developed wastewater

process has enabled an 80 % reduction in the freshwater intake to the bleaching process of the mill, and the mill wastewater discharge has decreased by 50 % (Joore et al. 2001; Ramaekers et al. 2001; Hepp et al. 2005). In Canada, at the pulp mill in New Brunswick, the evaporator condensate stream was identified to cause significant amounts of BOD and toxicity to the mill effluents, and a reverse osmosis membrane plant was installed to purify this stream and decrease the environmental load of the mill. The permeate of the membrane plant was recirculated to the bleaching process which lead to a 40 % reduction in water consumption (Webb 2002; Anon 2006).

Typically membrane filtration is used at pulp mills in treatment of bleaching effluents prior to the external biological treatment plant, because ultrafiltration improves the biodegradability of the effluent (see entry “► [Paper Pulp Production and Membrane Operations](#)”). The ultrafiltered bleaching effluent could be reused at the pulp mill for instance as washing water but it is often discharged through the biological treatment plant. The challenge in reuse of ultrafiltered bleaching effluents in pulp mill processes is that the permeates contain alkaline earth metals and there is a fear of them to accumulate and cause scaling problems in the circulation systems. Moreover, ultrafiltration does not retain chlorides and their accumulation might increase the corrosion risk in water circulation systems. If the effluents are nanofiltered, the risks caused by non-process elements are decreased, because their retention is higher in nanofiltration than in ultrafiltration. Thus, membrane filtration might enable safe water reuse at pulping processes when a membrane process producing water containing acceptable levels of non-process elements and organic compounds is chosen to be used.

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Water Sorption and Diffusion

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Separation processes occupy a critical place in process industries for isolation of products and recycling of reactants. Membrane technology has found immense prominence in solving challenging separation problems pertaining to wastewater treatment, drinking water purification, solvent

recovery, and gas purification. It has several advantages over conventional methods such as higher selectivity, low energy consumption, and moderate cost-to-performance ratio besides small footprint (Chapman et al. 2008). There are many situations where the target component cannot be separated by distillation, liquid extraction, and evaporation. The different membrane processes wherein water sorption and diffusion occurs are pervaporation, reverse osmosis, forward osmosis, ultrafiltration, nanofiltration, vapor permeation, microfiltration, and dialysis. Each process is dealt with in terms of membrane type, solubility, diffusivity, and effect of operating parameters on the properties.

Forward osmosis (FO): FO is another emerging membrane technology, which has several advantages such as low temperature and pressure requirements. FO process offers nearly complete rejection of a wide range of contaminants and possibly lower membrane fouling propensity compared to traditional hydrostatic pressure-driven membrane processes. As a result, FO process has been used extensively in wastewater treatment; seawater desalination; processing pharmaceutical, food, and dairy products; power generation; and protein enrichment. In FO, the feed and draw solutions are brought into contact through a semipermeable membrane as shown in Fig. 1. Due to difference in osmotic pressure ($\Delta\pi$) across the membrane, the solvent, usually water, flows from a region of higher concentration to lower solvent content. The osmotic pressure of a solution is commonly defined as

$$\pi = \frac{n}{V_m} iRT \quad (1)$$

where n is the number of solute molecules, V_m is the volume of pure solvent, i is the dimensionless van't Hoff factor, R is the ideal gas constant, and T is the temperature. In general, water flux (J_w) in FO process is given by the following relationship:

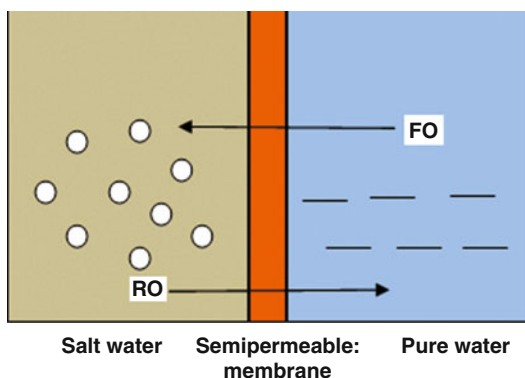
$$J_w = A\sigma\Delta\pi \quad (2)$$

where A is the water permeability of the membrane and σ is the reflection coefficient.

Water flux through the membrane mainly depends on choice of membrane material which allows passage of only water with retention of solute molecules type of draw solution used. Generally, membranes composed of a dense hydrophilic active layer casted onto a highly porous mesh-like substrate are usually employed. Figure 2 describes the mass transport of solvent molecules through thin-film composite (TFC) FO membrane from feed side to draw solution. External concentration polarization (ECP) occurs near the active membrane layer on the feed side, thus increasing the feed concentration from $C_{f,b}$ to $C_{f,m}$. As water permeates through the membrane, the draw solution gets more diluted and consequently concentration of the solute particles gradually

decreases at the membrane interface ($C_{d,m}$) when compared to bulk concentration ($C_{d,b}$) thereby leading to dilutive internal concentration polarization (ICP) within the porous support layer. The presence of both ECP and ICP results in lower osmotic pressure gradient across the active layer as against to bulk osmotic pressure difference.

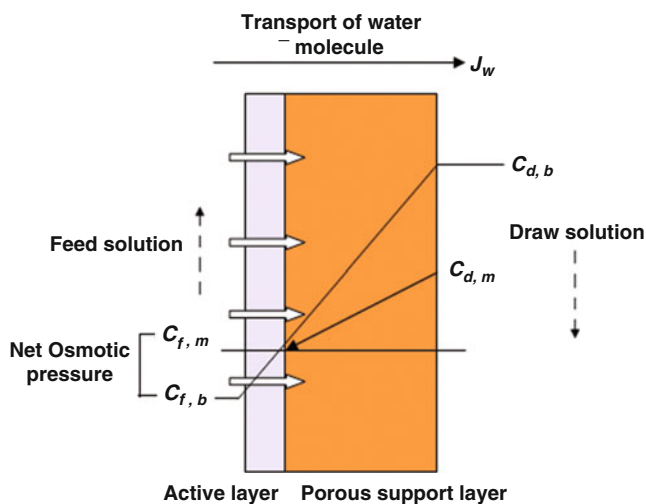
Reverse osmosis (RO): The principle of RO process shown in Fig. 1 illustrates the phenomenon of osmosis, osmotic pressure, and reverse osmosis. Osmosis is now also called FO to differentiate it from RO which is a more widely used process. RO is the application of an external pressure greater than the natural osmotic pressure of a feed solution to force water to flow from the feed solution side to the pure-water side through semi-permeable membrane. As a thumb rule, it can be stated that 1000 ppm of NaCl solution exerts an osmotic pressure of 0.7 atm which means that RO can occur only if the applied pressure is greater than 0.7 atm. Thus for seawater which contains 3.5 % w/v salts, the applied pressure must be greater than 25 atm. RO is a combination of membrane interfacial phenomenon and fluid transport under pressure through capillary pores. For providing freshwater, RO membrane separation technique plays an important role. In this process, raw water is passed through a semipermeable membrane using pressure as a driving force for removing impurities, organic contaminants, and salts for producing purified water. Basically two types of



Water Sorption and Diffusion, Fig. 1 Principle of RO and FO process

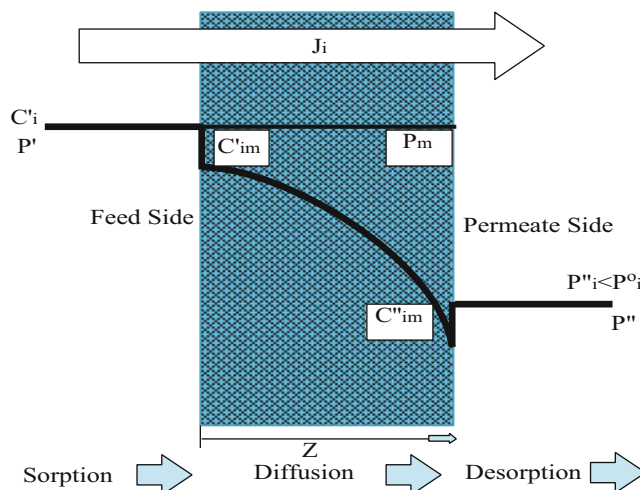
Water Sorption and Diffusion,

Fig. 2 Principle of water sorption and diffusion in FO process



Water Sorption and Diffusion,

Fig. 3 Principle of water sorption and diffusion in PV

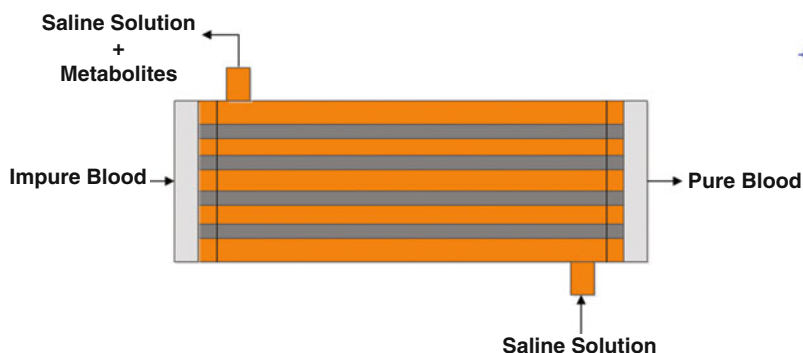
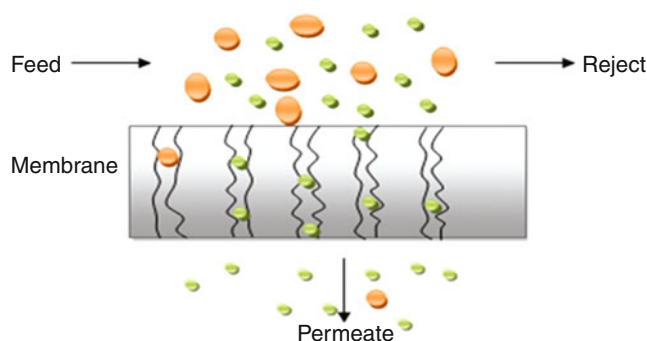


membranes have been used for RO, TFC and cellulose acetate membranes. During the preparation of TFC membranes by interfacial polymerization, a microporous polysulfone support membrane is further reinforced by a porous non-woven polyester backing layer. An ultrathin active layer of polymer film produced by interfacial polymerization is used to permeate water with rejection of salt. An important characteristic of TFC membrane is the sorption of water by the active layer. This is important because higher water sorption results in the membrane having greater water permeability. The selectivity of RO membranes has been correlated with the free volume of the active layer. Water sorption mechanism depends on both physical structure and chemical composition of the polymeric membrane. According to research, the transport of water molecules through a polymer at a temperature below its glass transition temperature is a three-stage process in which initially the water molecules get sorbed on to the membrane surface at the feed side, then diffuse through the thickness, and finally get desorbed on the permeate side. During diffusion some of the water molecules are bound to dense polymeric matrix leading to the swelling of membranes. In some cases, the kinetics of water diffusion mechanism can also be described successfully by Fick's law of diffusion. The water sorption occurs in the polymeric membrane due to the electrostatic attraction

between water and the functional groups of the polymers. The permeation rate is a function of solubility or the membrane separation factor which is a measure of the quality of separation that the membrane provides and diffusivity or the mass flux across the membrane. Solubility is a thermodynamic property whereas diffusivity is a kinetic parameter, both affecting perm selectivity (Mulder et al. 1985).

Pervaporation (PV) and vapor permeation (VP): PV membrane technique has exhibited tremendous potential for solvent dehydration, separation of azeotropes, close-boiling compounds, and organic–organic liquid mixtures. It can also be applied for recovery of small quantities of value-added compounds such as flavors and fragrances and removal of hazardous impurities, viz., volatile organic compounds (VOCs) such as vinyl chloride, benzene, and toluene from industrial effluents and for the enhancement of reaction yields in esterification and fermentation processes through continuous removal of water or the organic products. Figure 3 represents the principle of water sorption and diffusion in PV.

In PV, the liquid feed is maintained at a temperature close to its saturation point and then exposed to the membrane which allows one component, say water, to preferentially pass through the barrier. The downstream side of the membrane is kept under vacuum wherein permeating water is collected as vapor and then condensed. The

Water Sorption and Diffusion,**Fig. 4** Schematic diagram of dialysis process**Water Sorption and Diffusion,****Fig. 5** Principle of UF

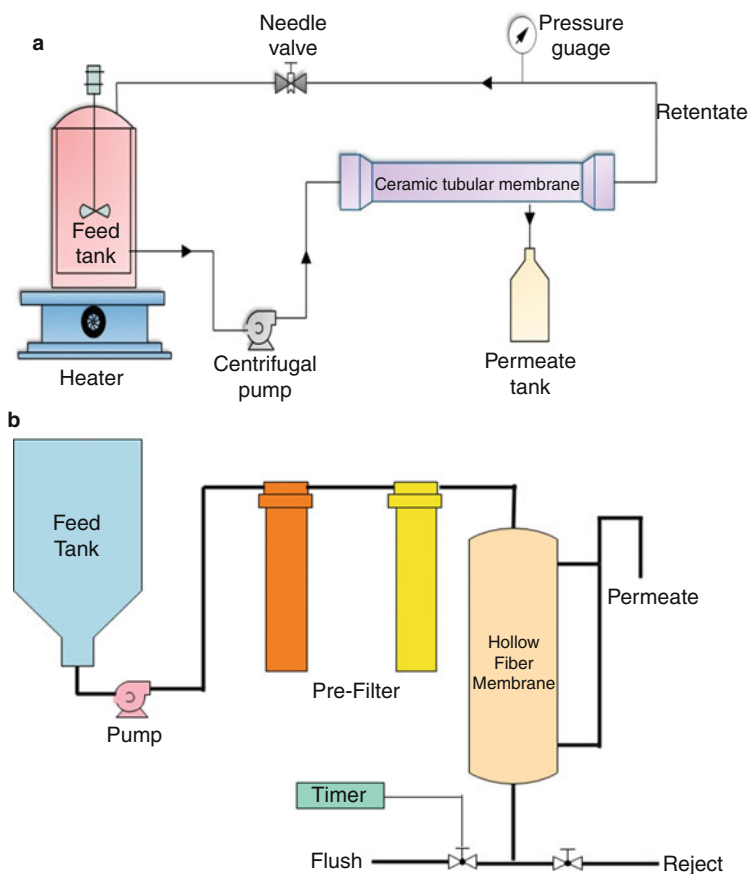
composition of this vapor is largely different from that produced by a conventional distillation process. The principle of VP is analogous to PV with physical state of feed being the only difference in the process. In VP, the feed is a mixture of vapors in saturated condition, and in PV, the feed is in liquid state. The driving force in PV is maintained through vacuum or an inert sweep gas in the permeate side. With absence of any phase change in VP, the additional cost of heat equivalent to the enthalpy of vaporization is not required. The other advantages of VP include the elimination of concentration polarization at the membrane surface.

Dialysis: This process involves the transportation of solutes and water due to concentration gradient across a porous membrane. The main application includes purification of blood by the removal of excess salts and water when the kidneys are malfunctioning. The other applications of dialysis are recovery of NaOH from cellulose-steeping liquors (Cooney et al. 1974) and removal of alcohol from beer. Figure 4 represents schematic diagram of dialysis process.

Ultrafiltration (UF): UF is used for the separation of macromolecules with lower operating pressure. UF membranes fractionate the components of a liquid predominantly in a pore size range of 2–200 nm. UF membranes are used to remove viruses, color, odor, and some colloidal natural organic matter. In this process, the feed is pressurized through the membrane to remove colloidal organic matter, viruses, color, and odor with a pressure ranging from 2 to 10 bar. The membrane acts as a filtering medium, allowing only dissolved substances of smaller molecular size than the membrane apertures to pass through them along with water. The other materials that cannot pass through the membrane are usually bigger compounds like enzymes, proteins, and antibiotics which get enriched in the retentate. The principle of the process is shown in Fig. 5.

Microfiltration (MF): The separation of very fine colloidal solids from a solution in the range of micro and sub-micrometer is named as microfiltration. Water present in the feed passes through the membrane, whereas fine suspended

Water Sorption and Diffusion, Fig. 6 (a) Ceramic MF membrane. (b) Laboratory MF/UF system



particles and colloidal impurities are retained. The pressure ranges from 0 to 2 bar and the pore size of the membrane ranges from 0.1 to 5 μm . The most important applications of MF include separation of water/oil emulsions, concentration of colloidal substances, and pretreatment in RO, NF, and UF systems. MF is also typically used for turbidity reduction and removal of giardia and cryptosporidium.

Different types of membranes are used for microfiltration such as polymeric and inorganic membranes which are present in different modular configurations such as spiral, tubular, hollow fiber, ceramic, and stainless steel. Figure 5 exhibits a ceramic MF module. An integrated MF/UF laboratory system is shown in Fig. 6 which is used for the pretreatment of domestic and industrial wastewater.

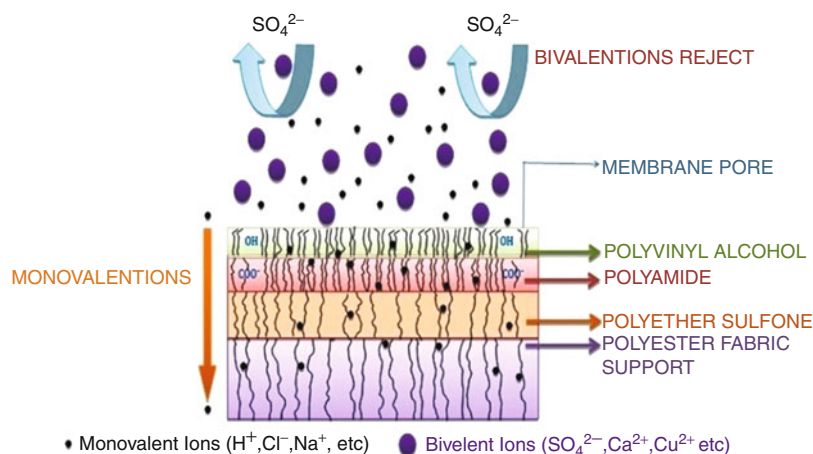
Nanofiltration (NF): This process allows monovalent salts to pass through the membrane

while retaining larger species such as multivalent salts. The pore size in a NF membrane corresponds to 0.5–2 nm. This process is extensively used in food and beverage industries for water purification. But its major application could be in the pharmaceutical industry since most commercial drugs have molecular weight cutoff in NF range. Additionally, NF application can be extended to solvent recovery provided solvent-resistant membranes are developed. The basic principle in which NF works is similar to UF, MF, and RO, but the distinguishing feature between them is their effective pore size and charge-based exclusion known as Donnan's principle. Reverse osmosis membranes reject all but the very smallest species, while MF allows considerably larger particles to pass through it as shown in Fig. 7.

To understand the mechanism of water sorption and diffusion in polymers, it is important to

Water Sorption and Diffusion,

Fig. 7 Principle of NF



analyze the transport phenomena happening within the membrane matrix (Maggana et al. 1999). In a membrane process, the polymer is usually kept in a moist environment, where water molecules along with low-molecular-weight substances can easily penetrate through to the other side even at room temperature, which brings about certain structural and physical changes.

But in perspective of enhancing the membrane performance, there is often a trade-off between selectivity and flux. Increasing one leads to a decrease in the other during performance modification. Regarding the performance, an index called the pervaporation separation index (PSI) is used which is expressed as selectivity $\times$ flux. Although this is an index useful in comparing different membranes, there could be instances wherein membranes, one having a low selectivity and high flux and the other with a high selectivity but low flux, can end up with the same PSI. Therefore, higher PSI is not an indication of superiority of a membrane. Separation performance also depends on appropriate membrane selection. Mainly, two classes of membranes are being used in most pervaporation operations: polymeric membranes and inorganic barriers. In polymeric membranes, organic polymer chains are cross-linked together, forming tiny voids between the segments through which molecules can diffuse. However, inorganic membranes have

increasingly become a focus of research due to several advantages over polymeric membranes such as solvent resistance and the ability to operate at higher temperatures since these are fabricated from ceramics or zeolites. By combining the advantages of both these two types of materials, a third class of membranes defined as composites are manufactured which consist of an organic polymeric membrane containing inorganic particles dispersed throughout. These are also commonly termed as mixed matrix membranes.

Membranes having a hydrophilic nature are generally used in dewatering of organic solvents through pervaporation (Lu et al. 2003). The component which comes out from the dense membranes follows a solution–diffusion process, and therefore, sorption of component in the membrane plays a major part in separation performance. The interaction between water and membrane is of high significance in hydrophilic membranes. Therefore, substantial research is going on to understand the mechanism of water sorption in hydrophilic polymers. Based on different studies, it is observed that when the polymer is in condensed state after the sorption of water, the mechanical and physical properties of the membrane change which enhances the mobility of the polymer chains and decreases the glass transition temperature, wherein water molecules play the role of a plasticizer. The hydrophilicity of a membrane is the measurement of the contact angle

between air and a drop of water on the membrane surface. This elucidates the degree of the material with respect to water. This measurement can also be made with respect to any solvent to be dehydrated to assist the membrane selection. Depending upon the contact angle between the solvent and the membrane, the nature of wettability allows water to preferentially get sorbed onto the membrane surface, forming an aqueous layer of resistance to mass transfer. This layer allows water to permeate through the pores but resists other components. By utilizing this behavior, various solvents can be dehydrated. According to Chapman et al. (2008), if the membrane is wetted by the solvent (water), then the solvent will enter and pass through the membrane, whereas for non-wetting solvents, additional pressure is required to be applied. For this, bubble-point procedure can be used to determine pore diameter and pore size distribution. In this test, the minimum pressure or bubble point at which the liquid is forced out of the membrane by an inert gas is determined. When the molecular sizes needed to be separated are relatively small such as low-molecular-weight solvents and water, then conventional processes like distillation are not effective due to azeotrope formation, close-boiling points, and high energy demands. A wide variety of membranes can be used for different types of applications. For the dehydration of solvents that contain smaller amounts of water, as compared to any other components, hydrophilic membranes are preferable to enable retention of the organic molecules. On the other hand, for separating small amounts of solvent from water, a hydrophobic membrane is more suitable (Madhumala et al. 2014). This choice ensures low running cost since PV is the only membrane process apart from MD which involves phase change and therefore high enthalpy of vaporization of either water (540 Kcal/kg) or the organic liquid. Dipole–dipole interactions, hydrogen bonding, and ion–dipole interactions between water and the membrane material are the basic forces involved in the hydrophilic PV.

To measure the sorption value of the hydrophilic membrane, small pieces of known weights are immersed in known concentrations of feed

solutions for time periods of 48 h each to enable membranes to reach equilibrium. After removing excess water, the membrane is weighed to determine the amount of water sorbed. The swelling degree is then calculated as follows:

$$DS = \frac{M_s - M_d}{M_d} * 100 \quad (3)$$

where M_s and M_d are the mass of the swollen and dry membranes, respectively. Organic concentration in membrane (Sunitha et al. 2013) is given by

$$\text{Organic concentration} = \frac{M_d - M_o}{M_s - M_o} * 100 \quad (4)$$

To further investigate the transport phenomena through the membranes, basic diffusion studies can be performed. According to Fick's law of diffusion, the ratio of the amount of liquid sorbed at a certain time t (M_t) to the amount sorbed at equilibrium (M_∞) depends on the square root of time:

$$\frac{M_t}{M_\infty} = \frac{4}{l} * \sqrt{\frac{D * t}{\pi}} \quad (5)$$

where M_t and M_∞ are the amount of solvent sorbed at time t and equilibrium, respectively. D is the diffusion coefficient and l is the membrane thickness. Sorption coefficient is determined by

$$S = \frac{M_\infty}{M_p} \quad (6)$$

The permeability coefficient (P) is the combined effect of both solubility (S) and diffusivity (D) which is calculated as:

$$P = D * S \quad (7)$$

Sunitha et al. (2013) reported a variation of swelling ratio with immersion time indigenously synthesizing membranes in eight different liquid mixtures. Table 1 shows some experimental results pertaining to degree of swelling and diffusion coefficient.

Water Sorption and Diffusion, Table 1 Literature data on water diffusion and flux of various membranes

S. no.	Process	Membrane type	Water diffusion coefficient (cm ² /s)	Water flux (kg/m ² h)	Separation application	Reference
1.	PV	NaAlg with guar gum-grafted polyacrylamide	1.49×10^{-9}	0.047	Water–acetic acid	Toti et al. (2001)
2.	PV	NaAlg/PVA	3.97×10^{-7}	NA	Water–isopropanol	Kurkuri et al. (2002)
3.	PV	CS/HSC	3.498×10^{-9}	NA	Ethanol–water	Jiraratananon et al. (2002)
4.	PV	NaAlg	1.34×10^{-8}	0.317	Isopropanol–water	Rao et al. (2008)
5.	PV	NaAlg/HEC-g-AAm	4.02×10^{-8}	1.113	Isopropanol–water	Rao et al. (2008)
6.	PV	Cross-linked PVA	1.2836×10^{-9}	0.05848	Ethylene glycol–water	Chen and Chen (1998)
7.	PV	PVA/TEOS	3.98×10^{-8}	0.0411	Water–acetic acid	Kulkarni et al. (2006)
8.	PV	PVA/TEOS	7.06×10^{-8}	0.0835	Water–acetic acid	Kulkarni et al. (2006)
9.	RO	Silica membranes	NA	9.5	Desalination	Muthia et al. (2013)
10.	NF	Polyamide/titania	NA	12.84	Desalination	Qiao et al. (2014)
11.	NF	Polyarylene sulfide sulfone	NA	64.99	Desalination	Ling et al. (2014)
12.	NF	SPPEs/PPES hollow fiber	NA	8.7	Desalination	Junnan et al. (2014)
13.	NF	Polyethylenimine/trimesoyl chloride	NA	24.5	Desalination	Dihua et al. (2014)
14.	MF	Ceramic membrane	NA	815	Wastewater treatment	Majouli et al. (2012)
15.	FO	PSf/SPPO	NA	39	Desalination	Zhengzhong et al. (2014)

SPPEs/PPES sulfonated poly(phthalazinone ether sulfone)/poly(phthalazinone ether sulfone), NaAlg sodium alginate, PVA poly(vinyl alcohol), CS/HSC chitosan/hydroxyethylcellulose
 PSf polysulfone, SPPO sulfonated poly(phenylene oxide)

Cross-References

- [Membranes for Solvent Dewatering](#)
- [Water Competitive Diffusion](#)

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Water Splitting

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Water splitting means a chemical transformation that separates water into its elements which are molecular oxygen (O₂) and molecular hydrogen (H₂). The transformation can be done by various processes such as electrolysis, photochemical, photocatalytic, thermal decomposition.

Electrolysis is a method of separating elements chemically bounded into compounds by passage of an electric current through them: in the case of electrolysis of water, the latter is decomposed (splitted) into gases O₂ and H₂. When energy is obtained from light, photochemical and photocatalytic devices can be used, and the system that splits water into hydrogen and oxygen is also named artificial photosynthesis (Devens et al. 2009).

Water splitting over a semiconductor photocatalyst using solar energy is a promising process for the large-scale production of clean, recyclable H₂ at temperatures close to the ambient one. Numerous attempts have been made to develop photocatalysts that function under visible light irradiation to efficiently utilize solar energy (Kazuhiko 2011; Valdes et al. 2012). The photocatalytic splitting of water under visible light irradiation is a greatly desired reaction system for hydrogen production. However, powdered photocatalysts always produce a gas mixture of hydrogen and oxygen in such a reaction, and thus, a separation process for the gas mixture is required before the hydrogen can be effectively utilized. Construction of a photocatalytic system enabling the separate

evolution of hydrogen and oxygen from water (e.g., by means of a membrane) under visible light irradiation and absence of sacrificial agents using a Z-scheme (Abe 2010) is, therefore, of vital interest. In this Z-scheme methodology, hydrogen and oxygen are generated photocatalytically in different cells that are illuminated and separated by a membrane. An electrolyte is used to ensure the electroneutrality in each cell and to allow charge transfer from one compartment to the other. One suitable electrolyte is the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pair. A Nafion membrane is a suitable barrier between the two compartments of the reactor because of its chemical and physical properties (Seger et al. 2007). The uptake characteristic of different cations (Fe^{3+} , Cu^{2+} , and Ni^{2+}) by Nafion 117 which is commonly used as separator for different chemical processes was also investigated (Ramírez et al. 2010).

Thermal decomposition (or thermolysis) is another approach for water splitting: it is a chemical transformation that breaks a substance into at least two chemical substances when heated. At elevated temperatures (e.g., 2200 °C), water molecules can decompose, but using catalysts, lower temperatures can be used to obtain hydrogen and oxygen.

Solar energy can be used for thermal decomposition of water via an integrated thermochemical reactor/receiver system (Agrafiotis et al. 2005). A multichannel honeycomb ceramic supports coated with active redox reagent powders, in a configuration similar to that encountered in an automobile catalytic converter, have been used. Iron-oxide-based redox materials, capable to operate under a complete redox cycle, could take oxygen from water producing pure hydrogen at reasonably low temperatures (800 °C) and could be regenerated at temperatures below 1300 °C. Ceramic honeycombs capable of achieving temperatures in that range when heated by concentrated solar radiation were assembled in a dedicated solar receiver/reactor. The operating conditions of the solar reactor were optimized to achieve adjustable, uniform temperatures up to 1300 °C throughout the honeycomb, making thus feasible the operation of the complete cycle by a single solar energy converter (Agrafiotis et al. 2005).

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Water Transport in Ion-Exchange Membranes

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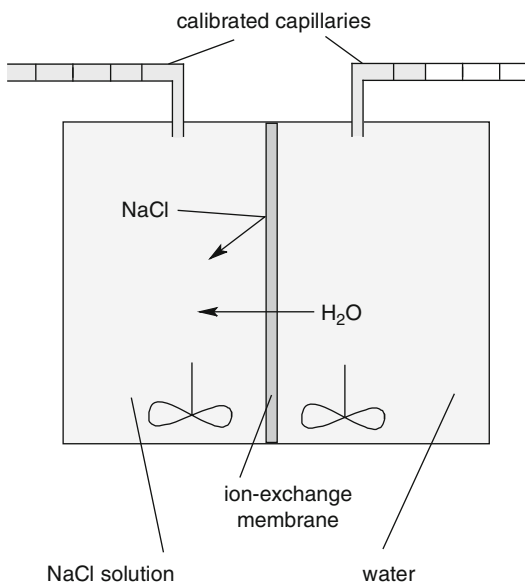
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The water transport through ion-exchange membranes is caused by osmosis and by



Water Transport in Ion-Exchange Membranes, Fig. 1 Schematic drawing illustrating the test cell for determining the osmotic water flux through an ion-exchange membrane

electroosmosis. The osmotic water transport is the result of concentration differences between the two solutions separated by the membrane. Electroosmosis refers to the water transported in the hydration shell of the ions migrating through the membrane due to an electrical potential gradient. The osmotic water transport is measured using a two-compartment cell containing pure water in one compartment separated by the membrane from the second compartment containing a salt solution. The volume change in the compartments is determined as a function of time in two horizontal capillaries connected with the compartments as indicated in the schematic drawing of Figs. 1 and 2, which illustrate the experimental setup to determine the water transport in osmosis and electroosmosis.

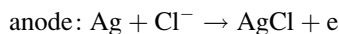
In osmotic water transport measurements, one cell is filled with water and the other with a salt solution. The water flux from the cell filled with water into that filled with the solution is measured in the horizontally arranged capillaries as indicated in Fig. 1. Since the osmotic pressure is a linear function of the concentration of a solution, the osmotic water transport increases linearly with the salt concentration.

The electroosmotic water transport is expressed by a transport number in analogy to the transport number of ions and is given by:

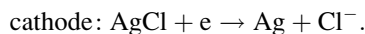
$$T_w^m = \frac{FJ_w}{i} \quad (1)$$

Here is the transport number of water through a membrane, F is the Faraday constant, i is the current density, and J_w is the water flux expressed in moles per unit area and time. In the electroosmotic water transport measurement, a direct current is applied using reversible electrodes, i.e., Ag/AgCl electrodes. Both compartments of the test cell are filled with a test solution of identical concentrations. The electroosmotic water transport of a cation-exchange membrane is a function of the migration of the cation and is determined by water connected to the ion in its hydration shell. The electroosmotic water transport through a cation-exchange membrane due to the migration of a Na^+ -ion can be determined by measuring the volume change in the two compartments of a test cell filled with a NaCl solution as indicated schematically in Fig. 2.

In the test it is assumed that the membrane is strictly semipermeable, i.e., it is only permeable for Na^+ -ions. However, the volume in the two compartments of the cell is not only the result of the water transport. The volumes of the cells are also changed by the electrode reactions. At the anode Cl^- -ions disappear and at the cathode Cl^- -ions are generated according to the following reaction scheme:



and



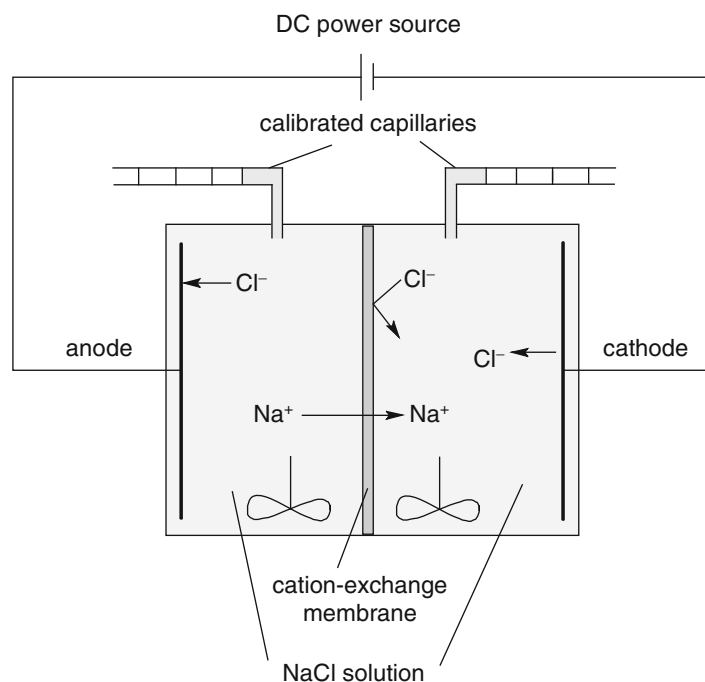
The electroosmotic water transport is calculated from the volume change in the two compartments:

$$\begin{aligned} \Delta V_F &= \Delta V_{\text{tot}} + \Delta \bar{V}_{\text{AgCl}} - \Delta \bar{V}_{\text{Cl}^-} \\ &= T_{\text{Na}^+}^m n_w^{\text{Na}^+} + \bar{V}_{\text{Na}^+} \end{aligned} \quad (2)$$

Here ΔV_{tot} and ΔV_F are the total volume change and the volume change, respectively, due to electroosmosis in the cell when electrical charges of

Water Transport in Ion-Exchange Membranes,

Fig. 2 Schematic drawing illustrating the test cell to determine the electroosmotic water transport



1 Faraday are transported, is the partial molar volume of AgCl and Ag, is the transport number of Na^+ -ions in the membrane, and is the number of water molecules carried by on Na^+ -ion.

The electroosmotic water flux is:

$$\Delta V_F = T_w^m \bar{V}_w \quad (3)$$

Here is the water transport number, ΔV_F is the electroosmotic water flux, and is the partial molar volume of water.

Different cations show rather different electroosmotic water transport numbers. Ions with a relatively large hydration shell such as the Na^+ -ion have a water transport number of 6–8. Protons have a very low water transport number of less than 3 because of the different transport mechanism which has been discussed earlier. The water transport number is decreasing with increasing salt concentration.

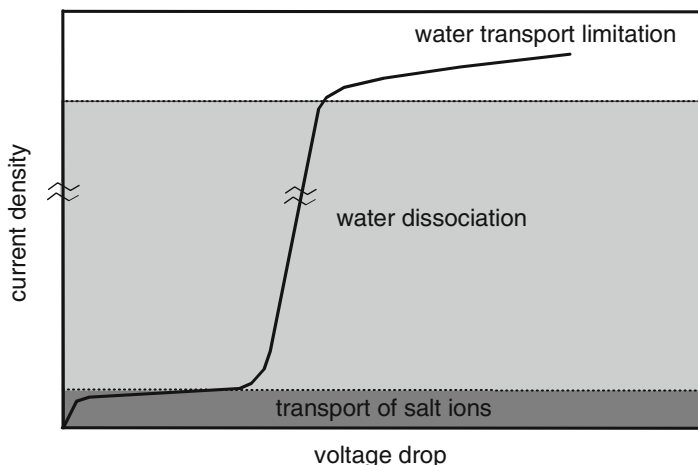
Characterization of Special Property Membranes

In many applications of electrodialysis and related processes, special property membranes are

required. For instance, for the pre-concentration of seawater for the production of table salt, membranes with a low permeability for divalent ions are required. In diffusion dialysis anion-exchange membranes with high proton permeability or cation-exchange membranes with high hydroxide ion permeability are needed, and in bipolar membrane applications generally acid and base blocking monopolar membranes as well as efficient bipolar membranes with a low electric resistance and good water dissociation capability are needed (Pourcelly et al. 1990). Most monopolar membranes can be characterized by applying the procedures described earlier. In addition to the electrical resistance and the permselectivity, the water dissociation capability is for bipolar membranes of prime importance. Therefore, membranes are generally characterized by a so-called current versus voltage plot. Determination of the current through a bipolar membrane as a function of the applied voltage provides information about the water dissociation, the electrical resistance, and the salt leakage of the membrane. A typical current versus voltage curve of a commercial bipolar membrane is shown in Fig. 3 (Krol et al. 1998).

Water Transport in Ion-Exchange Membranes,

Fig. 3 Current density versus applied voltage curve schematic drawing indicating three distinct areas where the current is determined by the salt transport, the water dissociation, and by the water diffusion into the reaction zone of the membrane



As illustrated in the schematic drawing, three distinct areas in the current versus voltage curve can be identified. The first area is characterized by a linear increase in current with the applied voltage until a limiting value of ca. 1 mA cm^{-2} is reached at ca. 0.1 V. A further increase in the applied voltage does not lead to an increase in the current. The current in this region is the result of salt transport from the transition region of the bipolar membrane into the outside solutions due to the driving force of the applied potential. Up to an applied voltage of ca. 0.1 V, this transport is compensated by salt diffusion from the outside solutions into the bipolar membrane due to a concentration gradient. The salt transport out of the membrane cannot exceed the diffusive salt transport into the membrane independent of the applied voltage. Thus, a steady state is reached and the current is limited by the salt diffusion into the membrane until the voltage drop across the membrane reaches 0.6–0.8 V. The drastic current increasing when the applied voltage is increased further is the result of the transport of H^+ and OH^- ions that are produced within the bipolar membrane. In the region between 0.5 and 1.2 V applied voltage and a current density of up to 500 mA cm^{-2} , the current is carried by H^+ and OH^- ions which are provided by the water dissociated. If the applied voltage has reached ca. 1.2 V, a further increase does not lead to a significant increase in current. This limitation of the current density is the result of a decrease in the H^+ and OH^- ion

concentration in the transition region of the bipolar membrane which is limited by the water diffusion rate from the outside phases into the membrane. Operation of the membrane in the third, i.e., the water diffusion limited region, generally leads to a destruction of the membrane (Krol et al. 1998).

In addition to determining the current density as a function of the applied voltage more complex testing methods such as impedance spectroscopy (Zabolotsky et al. 1978; Holdik et al. 1998) or chronopotentiometric measurements (Wilhelm 2001) are used to obtain more detailed information about the mechanism of the water dissociation and the resistance of the bipolar membrane.

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Water Treatment by Electrodialysis

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Clean water, free of toxic chemicals and pathogens, is essential to human health (Montaña et al. 2013). Treatment processes for the production of freshwater from any kind of water sources such as groundwater and surface water, as well as recycled process and wastewater, are becoming more and more important to cope with rapidly increasing water demand. Increased nitrate concentrations, mainly caused by non-clarified wastewater or excessive application of artificial fertilizer and manure in agriculture, are found quite often in groundwater. Also many surface waterworks are confronted with the necessity to remove dissolved ionic substances. Common treatment methods used at waterworks are a combination of chemical oxidation, coagulation-flocculation, sand filtration, and disinfection. However, in recent years, membrane technology has become an extraordinarily useful tool for the production of freshwater. Recent advances suggest that many issues involving water quality could be resolved or greatly ameliorated by using ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), or electrodialysis reversal (EDR) processes (Montaña et al. 2013).

UF and NF membrane filtration processes work by excluding contaminants using pore-size constraints when water under pressure is forced to pass through a semipermeable membrane with different pore sizes. The RO membrane works as a molecular filter that rejects positively and negatively charged ions based on molecular weight when pressurized water is forced through the

membrane (Montaña et al. 2013). In contrast, the driving force for separation in ED and EDR processes is an electric potential, and an applied current is used to transport ionic species across selectively permeable membranes. The principal difference between ED and EDR is that EDR includes the additional step of a change in electrode polarity every 15–20 min, thus causing a reversal in ion movement. This step minimizes scale buildup on the membranes which means that EDR can operate for longer time periods between cleanings (Montaña et al. 2013).

Treatment processes are required, which are reliable, selective, easy to operate, and have low costs. Electrodialysis fulfills these requirements quite well. The special features of electrodialysis are high water recovery, selectivity, low chemical demand, and low energy demand (Hell and Lahnsteiner 2002).

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Water Treatment by Membrane Operations

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Water treatment by membrane operations covers a wide field of technologies and processes related to the treatment of municipal, agricultural and industrial wastewater, water purification, desalination, water recovery from wetlands, and remediation of contaminated soil.

In all cases the motivation to treat wastewater is given by the concurrent scarcity of freshwater and the increasing demand for it by a growing world population. Furthermore, the increase in human population has cascading effects on water availability and treatment with agriculture and industrial use polluting groundwater and high population concentration in cities producing ever-larger volumes of waste to treat. In all these instances, membranes play a key role in controlling the composition of the treated water stream, via the removal of toxic substances and the recovery of water for reuse. This can be attributed to the ability of membranes, with the appropriate pore or MWCO size, to provide an effective barrier to any contaminants present in the water to treat. As the size of these contaminants, from ions to bacteria, varies several orders of magnitude, water treatment plants often contain several membrane processes in series with decreasing MWCO.

Microfiltration (MF) and ultrafiltration (UF) membranes are mainly employed to remove solid particles and microbes/bacteria (Cheryan 1998). These are often used as a pretreatment step for nanofiltration (NF) and reverse osmosis (RO) membrane processes that can remove natural organic matter, viruses, and ions (Van Der Bruggen et al. 2003). Each stage is complemented by a host of other treatment processes (e.g., mesh screening, coagulation, UV disinfection, ozonation, etc.). An example of an integrated membrane process is represented by membrane bioreactors (MBRs), where a biotreatment process to degrade suspended organic matter is coupled with a membrane to retain the biomass, producing a clarified and disinfected effluent (Judd 2011). MBRs are rapidly supplanting legacy activated sludge treatment plants for municipal wastewater due to a smaller footprint, reduced use of chemicals, and superior quality of the treated water (Leiknes 2009). Current MBR plants employ UF membranes with NF ones being currently assessed as they can also remove viruses and some organic molecules,

reducing the need for further treatment downstream. Membrane fouling remains the main obstacle toward more widespread adoption of MBRs as it requires expensive gassing and chemical cleansing to avoid dramatic flux reductions caused by the formation of biofilms on the membrane feed side. Another example, in earlier stages of development compared to MBRs, is the coupling of a membrane with oxidation of pollutants via photocatalysis (Romanos et al. 2013). This approach has significant potential as the organic pollutants can be fully mineralized into water and carbon dioxide, producing no sludge nor requiring chemical cleansing. The long-term activity and stability of the photocatalyst remains the challenging aspect of this promising technology.

Nanofiltration membranes in water treatment are mainly used for softening water, the reduction in the concentration of calcium and magnesium ions, particularly groundwater. Typically, thin film composite membranes are used, though the high pressures required somewhat limit their use. NF membranes are also effective at removing natural organic matter, viruses, and pesticides, the latter of particular importance for treatment of agricultural waste (Van der Bruggen and Vandecasteele 2003).

Reverse osmosis membranes often represent the so-called polishing step in water treatment, thanks to the ability to remove dissolved ions as well as arsenic and small organic molecules (Van Der Bruggen et al. 2003). RO membranes are also very effective at removing nitrates originating from the intense use of fertilizers in agriculture. Rejection of boron by RO membranes remains low under typical operating conditions. RO membranes are also the technology of choice for obtaining freshwater from sea- and brackish water, at the cost of significant energy expenditure to force the saltwater through the membrane. Furthermore, RO membranes require extensive pretreatment steps to remove solids, particulate, and organic matter (Voutchkov 2013). Some RO membranes also require dechlorination of the feed

to prevent swelling of the membrane selective layer with consequent loss of ion rejection.

Nitrates, present in agricultural waste as a consequence of the use of pesticides and in some manufacturing waste streams, are highly toxic and difficult to remove as they are water soluble and do not bind to soil. Membrane denitrification has been extensively investigated. RO membranes are capable of removing nitrates below legal limits but high running costs and require the remineralization of the treated effluent before it can be released. Since nitrates are monovalent ions, NF membrane can only remove a fraction of them and has been used as a first step before RO, obtaining lower overall costs (Van der Bruggen and Vandecasteele 2003). MBRs, using UF membranes, have also proven to be effective and economical at denitrification (McAdam and Judd 2006).

Sulfates are present in water streams originating from a variety of sources, including waste streams from pigment and clothing industries, mining, as well as municipal gray waters as part of shampoos and detergents. They also can originate from coal combustion, leading to acid rain, though this source has been significantly reduced in the last 30 years.

Nanofiltration is the method of choice to remove sulfates and is extensively used in industry (Košutić et al. 2004), for example, in treating waste from chlorine production plants containing sodium sulfate or treating waste produced by consumer product manufacturers (Gawaad et al. 2011). Waste containing high percentages of sulfates from gold and coal mining in South Africa has also been successfully treated using NF membranes.

Phosphorous compounds are present in high concentrations in the waste streams of several industries, including detergent manufacturing and metal coating processes. Left untreated, the high phosphorous leads to an overgrowth of algae in the sea, leading to the formation of dead zones where no fish are present due to a lack of available oxygen in the seawater. A well-known example of this phenomenon is in the Gulf of Mexico at the estuary of the Mississippi River. RO membranes

are effective at removing phosphorous compounds as well as nitrates and ensuring high-quality water at a high cost. A more effective solution is the use of crossflow microfiltration processes, sometimes used in conjunction with iron-based precipitants (Dittrich et al. 1996).

Fluoride is naturally present in groundwater and a certain content (~0.5 ppm) is necessary to protect the teeth, whereas higher concentrations have adverse health effects. Nanofiltration is the method of choice to regulate fluoride concentration in drinking water (Choi et al. 2001), as it does not require the remineralization step necessary when using RO. Electrodialysis has also been successfully employed to produce drinking water with low fluoride concentration (Amor et al. 1998), though NF has been found to be more effective.

Cross-References

- ▶ [Membrane Bioreactor](#)
- ▶ [Microfiltration \(MF\)](#)
- ▶ [Nanofiltration](#)
- ▶ [Ultrafiltration \(UF\)](#)

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atomically smooth and chemically homogeneous. Conversely, very few solids are atomically flat. Wetting on rough surfaces was first considered by Wenzel (1936). In the Wenzel state, where the roughness grooves are completely filled with liquid, the contact angle (θ_w) can be described by

$$\cos \theta_w = R_f \left[\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right] \quad (1)$$

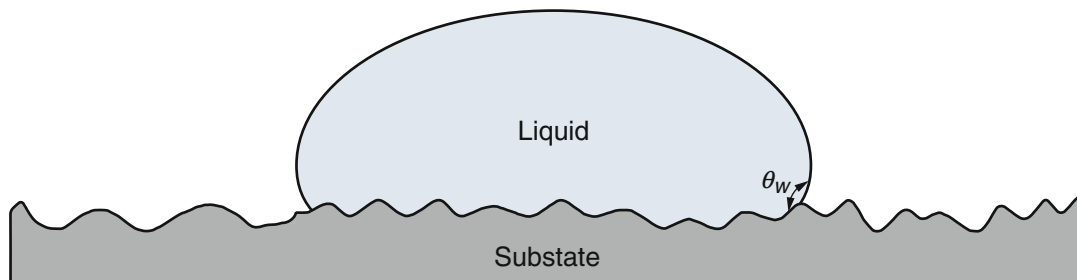
where R_f is the surface roughness factor, which is defined as

$$R_f = \frac{\text{Actual area}}{\text{Projected area}} \quad (2)$$

Combining Wenzel equation with Young's equation yields

$$\cos \theta_w = R_f \cos \theta_C \quad (3)$$

Since the roughness factor is always larger than unity in practical situations, it is obvious that the apparent angle on a roughened surface will become smaller if its intrinsic contact angle on a smooth surface is less than 90° . Similarly, the apparent contact angle will be larger, if its intrinsic contact angle is larger than 90° (Fig. 1).



Wenzel Model, Fig. 1 Liquid droplet on a rough surface. The contact angle can be predicted by Wenzel model (Hsu 2010)

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Wet Chemistry Method for Ceramic Membrane Preparation

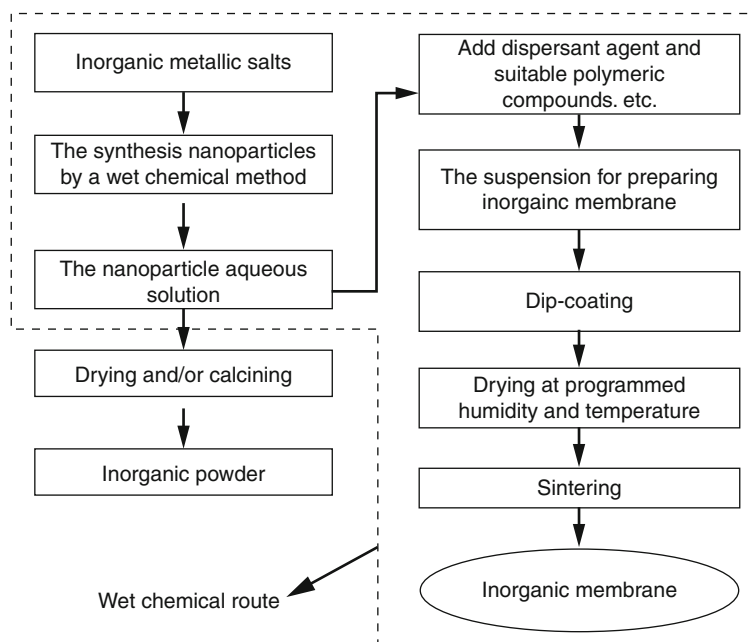
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The **wet chemistry method for ceramic membrane preparation** is a method to fabricate ceramic ultrafiltration membranes directly derived from the nanoparticle suspension that was the intermediate product prior to drying and calcination in the synthesis of nanoparticles (Fig. 1). Traditionally, ceramic ultrafiltration membranes

are usually produced by the sol-gel method, for which sensitive control is required and the reagents used impact environment. Wet chemical method was developed as an alternative for ceramic ultrafiltration membrane preparations (Ding et al. 2006). This technique was developed based on the state-particle-sintering process, which is an alternative for ceramic ultrafiltration membrane preparation (Cortalezzi et al. 2003). The state-particle-sintering method faces a problem that nanoparticles are easy to grow and form aggregates during the drying and/or calcination and it is very difficult to disperse these aggregated nanoparticles. The wet chemical method directly derives ceramic filtration membranes from the nanoparticle suspension that was the in-process product prior to drying and/or calcination in the synthesis of nanoparticle. This procedure begins with suspension which is the in-process product prior to drying and/or calcination in the nanoparticle synthesis. Thus, the nanoparticles exist entirely in an aqueous environment prior to forming a coating layer by dip coating and do not have an intractable problem of dispersion (Ding et al. 2006).

Wet Chemistry Method for Ceramic Membrane Preparation, Fig. 1 Wet chemical route



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Whey Demineralization with Membrane Operations

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There are various reasons for demineralization in whey processing. Minerals in whey cause issues including (Daufin et al. 2001):

- Slow lactose crystallization
- Fouling in MF and UF used for producing protein concentrates and isolates
- Nutritional imbalance in human and infant foods

Demineralization is therefore advantageous in whey processing for various performance and product reasons. Generally, minerals affect the flavor, functionality, and value of whey products justifying the use of demineralization systems. Electrodialysis (ED), ion exchange (IE), and nanofiltration (NF) are well-known operations achieving demineralization of 25–95 % (Daufin et al. 2001; Greiter et al. 2002). ED and IE are considered costly to operate in terms of equipment and running costs and produce large volumes of waste effluent that must be treated (Daufin et al. 2001). NF has advantages over ED; for example, it is more selective to separate

monovalent ions over divalent ions. Also, this selectivity is not as significantly altered as in ED, which is impacted by protein adsorption on the membranes due to the applied electrical field. The fouling can be managed by separation of concentrate loops to two different loops, and pulsed electrical fields can minimize fouling; however, the compromise is increased processing times (Casademont et al. 2009). Losses of lactose and proteins are lower in NF than in ED and IE, respectively. NF is therefore showing promise as a process to be more cost-effective, particularly in terms of reduced energy consumption, but can only achieve partial demineralization (Brans et al. 2004; van der Horst et al. 1995).

Major applications of demineralization address the three issues listed above, and is being utilized during processing of whey streams as part of lactose crystallization. In this application, lactose is depleted of minerals by NF prior to sending to the crystallizers. The demineralization step leads to higher lactose yields (Daufin et al. 2001), where solid lactose is produced. Refined lactose is valuable in the production of baby foods, sweets, baked goods, sauces, and dressing (Henning et al. 2006). In concentration of whey, ED is used for demineralizing UF concentrate to produce whey protein concentrate (WPC). The WPC (35–80 % protein) after demineralization is mixed with lactose and nonfat milk solids in the production of infant formula (Bazinet 2004). To produce demineralized and delactosed WPC, crystallization and separation of lactose are performed prior to demineralization by ED or IE (Henning et al. 2006). Lactose and mineral depleted WPC is evaporated and dried to produce whey protein powder.

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nonprotein nitrogen (Hausmann et al. 2013; Jelen 1979). Whey has previously been regarded as a waste by-product in cheese making, but due to the high organic content of whey, disposal to the environment led to environmental and health issues where it added a nutrient burden to natural waterways and facilitated the growth of infectious organisms. With the introduction of membrane technologies to the dairy industry over the last three decades, whey waste is now cost-effectively processed into valuable products and is an example of how an industry has successfully dealt with a waste problem in a commercially viable way. Products that utilize whey include body-building formula, while other examples include its use as a food ingredient, for example, whey proteins replacing egg proteins in confectionary and bakery products and milk in ice cream and other dairy products.

Whey Processing: Overview and Role of Membranes

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Whey Production, Its Composition, and Market Value

Whey is the by-product of the manufacture of cheese, which can vary depending on the type of cheese. For example, whey can be found in “sweet,” “acid,” and “salty” forms depending on what type of cheese is being produced or where in the production the whey is removed (Ramchandran and Vasiljevic 2013). Whey can be generally regarded as milk without casein and fat (Daufin et al. 2001). An example of solids in whey (i.e., non-water components) consists primarily of lactose (75–80 %), minerals (9–10 %), and whey protein (8–11 %). The remaining components in whey include fat, casein, and

Overview of Membranes for Whey Processing

Membrane technology has played a major role in the development of modern dairy processing. Forty percent of all membranes used in the food industry are for dairy application (Daufin et al. 2001). The majority of the membranes in dairy are used for whey processing (Pouliot 2008). The membranes have been applied in numerous roles including producing desired products of reliable quality or even extracting specific proteins (Henning et al. 2006). However the focus here is in whey processing. The membrane technologies that can be used to process whey involve every type of membrane filtration size classification: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The majority of membranes used in whey processing are UF and RO, where UF is the most popular (Pouliot 2008). Figure 1 shows the simplified flow diagrams of how membrane operations function in whey processing. Each type operates to fractionate the core components of whey in the order of fats (MF), proteins (UF), lactose (NF), and minerals (RO). Because RO removes water, it is applied on both the concentrate of UF and the permeate of NF.

Membranes come in a wide range of materials and geometries. Materials include polymeric, ceramic, and metallic. The geometries include tubular, hollow fiber, and flat sheet. Flat-sheet membranes are usually configured into spiral wound and plate and frame modules. Spiral wound membrane modules are the most common in whey processing and are predominantly made of polymeric materials. Polymer membranes are low cost and compact. Ceramic membranes are also popular in dairy processing due to their food compatibility, long life, and unique narrow pore size distribution giving them the ability to target specific components which are desired to be separated. Each filtration operation is described in the following sections.

Whey Microfiltration

MF is commonly applied in dairy processing as a means to remove fat globules but also has a function to remove microorganisms as small as bacteria for extending shelf life of dairy products (Daufin et al. 2001). MF is defined by its pore size ranging from 0.1 to 5 μm . For fat separations, MF can be chosen based on pore size to fractionate large and small fat globules being of use in various dairy products. For bacteria removal, a

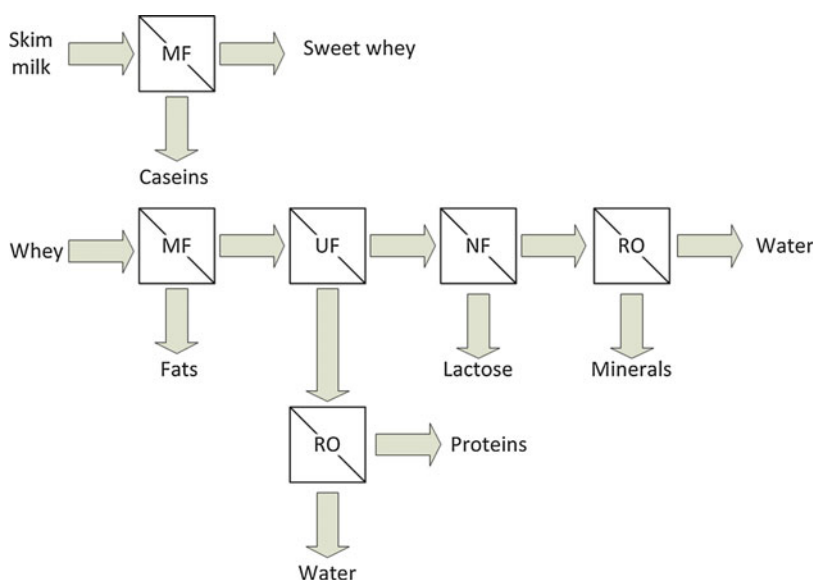
membrane with pore size of 1.4 μm can retain 99.0 % bacteria, while casein transmission is 99 %. The application for processing whey as shown in Fig. 1 (bottom train) has been proposed using ceramic membranes for removing fats to prevent fouling of the downstream UF membrane (Golbandi et al. 2013). This allows for higher protein concentrations to be achieved by UF (Ramchandran and Vasiljevic 2013). MF can also be used to produce sweet whey from skim milk as shown in the top train of Fig. 1. Ceramic MF membranes with pore size of 0.1 μm can be used to process skim milk, producing a product having similar composition to sweet whey. Aside from the process trains in Fig. 1, MF can also be used to concentrate native caseins which are used in the cheese-making process (e.g., for its excellent rennet-coagulating properties). It is this ability for MF to reduce the ratio of whey proteins to caseins in cheese milk that is gaining attention due to its ability to improve yield of cheese, particularly hard cheese varieties.

Whey Ultrafiltration

UF is defined in terms of its pore size, which ranges from 0.001 to 0.5 μm (Pouliot 2008). UF is one of the most commonly used membrane

Whey Processing: Overview and Role of Membranes,

Fig. 1 Membrane filtration operations used in cheese making or whey processing. *Top train* gives an example of MF to produce a permeate resembling sweet whey. *Bottom train* gives an example of whey-processing membrane filtration operations



processes used in dairy and will be presented in more detail in the next section “[Whey Ultrafiltration](#).” Its primary function in whey processing is to concentrate whey proteins, leading to whey protein concentrate (WPC), being a valuable product in many markets.

Whey Nanofiltration

NF is a newer membrane separation to industry, which has the ability to enable minerals to pass but concentrate larger organic molecules. Its pore size is in the range of 0.1–1 nm (Pouliot 2008) which is in the size range of small molecules and minerals. In some types of NF, minerals can be fractionated (i.e., passing monovalent salts like sodium chloride but blocking multivalent salts like calcium phosphate). However, as shown in Fig. 1, a common application in whey processing is to process UF permeate. The UF permeate, depleted of fats and proteins, is processed by NF to concentrate lactose and permeate minerals. The concentrated lactose fed to lactose crystallizers increases the lactose yield (Daufin et al. 2001). NF application in demineralization will be discussed in more detail in the section “[► Whey Demineralization with Membrane Operations](#).” Another application of NF is in the conversion of acid whey into sweet whey involving pH adjustment and diafiltration (Pouliot 2008).

Whey Reverse Osmosis

RO can be regarded as concentrating essentially everything and permeating only water, which means it blocks essentially all the smallest molecules in solution corresponding to a pore size of <0.1 nm (Pouliot 2008). In dairy processing, RO is regarded as a dewatering operation that is less energy intensive than evaporative techniques. RO is mostly used for whey concentration (Daufin et al. 2001). Here, whey is concentrated up to 27 % dry matter at which osmotic pressure of the whey becomes limiting and must be passed to an evaporative process if continued drying is needed. RO also becomes limiting at high dry matter

concentrations due to high viscosity, lactose crystallization, and calcium phosphate precipitation. The ability to extend this limit for whey processing has been explored with membrane distillation, where energy and performance advantages could be realized due to lower pressure required (Hausmann et al. 2014). RO can also be applied to treat NF permeate as shown in Fig. 1. Here, most organic matter has been removed and the RO operates to concentrate dairy minerals. No significant market has been found for dairy minerals concentrated by RO, so at present the RO is useful to reduce the volume sent to brine lagoon as a sewer or ocean outfall is not convenient or viable at the site the dairy plant is located. As shown in Fig. 1, RO can also be used on the UF concentrate to dewater the proteins prior to drying, which can save energy as thermal processes utilize much more energy overall than RO.

Electrodialysis

Electrodialysis (ED) is an electrochemical separation process where ionic species are transported from one solution to another under the influence of an electrical charge. In migrating from the solution, the ions pass cationic and anionic membranes, giving the process the ability to demineralize the incoming solution. ED is used in food processing to concentrate, purify, or modify foods (Bazinet 2004). The key distinction of ED to MF, UF, NF, and RO is that ED uses an electric field as the driving force for separation, thus selecting species having charges. The other operations worked principally on size exclusion and require pressure as the driving force. ED is a well-known process in dairy processing, having roles including demineralization, deacidification, acid production, and enriching protein fractions. Demineralization of whey is an important application of ED, as the mineral salts affect the flavor, functionality, and value of whey products. This will be explored in more details in the section “[Whey Demineralisation and Membrane Operations](#).”

While not shown in Fig. 1, ED is applied in various locations in whey processing train. It can

be applied to both the permeate and concentrate of UF, but work appears mostly done by researchers and little application in industry (Bazinet 2004). In the application to UF concentrate, ED can have an important role in the production of whey protein concentrate. The concentrate is demineralized by ED and mixed with lactose and nonfat milk solids to produce infant formula. In the application of deacidification, ED can be used to remove organic acid (e.g., lactic acid) produced during the fermentation of whey. More details of this aspect of whey processing can be found in the literature (Bazinet 2004).

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Whey Protein Concentrate: Overview and Membrane Operations

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Due to the ever-increasing production of cheese varieties, the generation of whey, as a consequence, results in the separation, fractionation, and concentration of valuable whey components, mainly proteins, while other components such as lactose and specific minerals are also extracted and used in different industrial applications. The estimated world's whey protein production exceeds 770,000 metric tonnes annually (Thompson et al. 2009). The composition of whey protein products usually varies depending on the method of casein concentration. The whey resulting from rennet-coagulated casein or rennet-type Cheddar or Swiss cheese manufacturing is known as sweet whey (pH >5.6). It contains higher lactose content than acid whey, which is obtained from the manufacture of acid casein brought about by addition of either lactic or mineral acid. It also contains more mineral (ash) content comparatively. Once a major pollutant, whey has now been recognized as a source of a diverse range of products including whey powder, sweet whey, demineralized whey, deproteinized whey, nonhygroscopic demineralized whey, reduced lactose whey, lactose, whey protein concentrates, whey protein isolates, and a range of different individual proteins with various physical and physiological functionalities. Based on this list, whey-based products may be grouped into three classes – basic products (whey products and variants), value-added products (whey protein concentrate and isolate), and specialized products (lactoperoxidase, lactoferrin, whey

protein-derived peptides, and nutraceuticals) (Kilara 2008). Value-added whey products are protein-enriched fractions containing from 25 % to over 90 % of proteins. The nonprotein fraction is composed of water and varying concentration of lactose, minerals, minute amounts of lipids, and likely organic acids produced during metabolic activity of cheese starter cultures. The overall functionality of concentrated whey proteins depends on the initial composition of whey. Whey proteins are a complex mixture of various proteins present in different concentrations. The bovine whey is composed of β -lactoglobulin (β -Lg), α -lactalbumin (α -La), bovine serum albumin (BSA), immunoglobulins (Ig), proteose peptones, and some other minor proteins including lactoperoxidase, lysosome, and lactoferrin. β -Lg is the most abundant whey protein with the molecular weight of ~ 18.3 kDa with the primary sequence composed of 162 amino acids. Its isoelectric point is $\sim$ pH 5.2 representing ~ 50 % of total whey proteins and also ~ 12 % of total milk proteins. Ten genetic variants of bovine β -Lg have been identified so far (Fox and McSweeney 2003); however, the two common variants with equal frequency are β -Lg A and β -Lg B, which differ from each other only in two amino acids, resulting in a significant difference in their solubility (de Wit 2009). The next important variant is variant C, identified in Jersey cows. Depending on the positioning of different amino acids and salt bridges on the protein, the heat stability of these β -Lg genetic variants differs. For example, at low temperatures, variant A is less stable than variant C as opposed to stability at higher temperatures, at which variant A is more stable than variants B and C due to its better hydrophobic packing. The major features of the secondary structure of β -Lg are two antiparallel β -sheets formed by nine strands labeled A to I, and eight of them form somewhat flattened β -barrel, which covers the thiol group of Cys₁₂₁ with the help of α -helix that is situated parallel to strands A, F, G, and H. Furthermore, one side of both the β -sheets is hydrophobic, and the hydrophobic sides face each other forming a highly hydrophobic cavity

(Considine et al. 2007). The stability of the ternary structure of β -Lg is strongly depending on the two disulfide bonds positioned between Cys₆₆-Cys₁₆₀ and Cys₁₀₆-Cys₁₁₉ (Thompson et al. 2009). They are available as dimers between pH ~ 3 and ~ 7.5 , and as a result, at natural pH they exist as stable non-covalent dimers at room temperature, but beyond that temperature they dissociate to monomers. α -La represents ~ 20 % of total whey proteins and ~ 3.5 % of total milk proteins. It is composed of 123 amino acid residues with the molecular weight of ~ 14 kDa and the isoelectric point of $\sim$ pH 4.8. Two genetic variants of α -La have been identified as A- and B- (Fox and McSweeney 2003). This globular molecule has split into two as an α -lobe, which contains three α -helices (about 26 %) and two short helices, and a β -lobe that contains small three stranded β -sheets (about 14 %) and a short helical structure; however, 60 % of the protein is unordered (Thompson et al. 2009). In the native form, α -La is a monomer with four disulfide bridges between the amino acid residues of 6 and 120, 28 and 111, 61 and 77, and 73 and 91. However, the disulfide bond between Cys₆ and Cys₁₂₀ is more sensitive to be affected than the other three due to its lower inherent stability (Considine et al. 2007). Meanwhile, the absence of thiol groups in the molecule makes it somewhat heat stable. It has a stable configuration between pH 5.4 and 9 (Fox and McSweeney 2003). In addition, it has a Ca²⁺-binding site located in the cleft of two lobes via Asp residues, and Ca also promotes the unfolding of α -La, which means, again, the promotion of heat stability and also recovery of the native conformation. α -La is the most heat stable of the main WP (Fox and McSweeney 2003). Proportionally the third largest whey protein, bovine serum albumin (BSA), consists of 582 amino acid residues with a molecular weight of ~ 66 kDa. Its isoelectric pH is ~ 5.3 . The protein has a multi-domain (three) structure with complex ligand-binding ability. The domains are stabilized by 17 intramolecular disulfide bonds and one free thiol group at Cys₃₄ residue (Thompson et al. 2009). It does not contain any β -sheet; instead it is composed of mainly

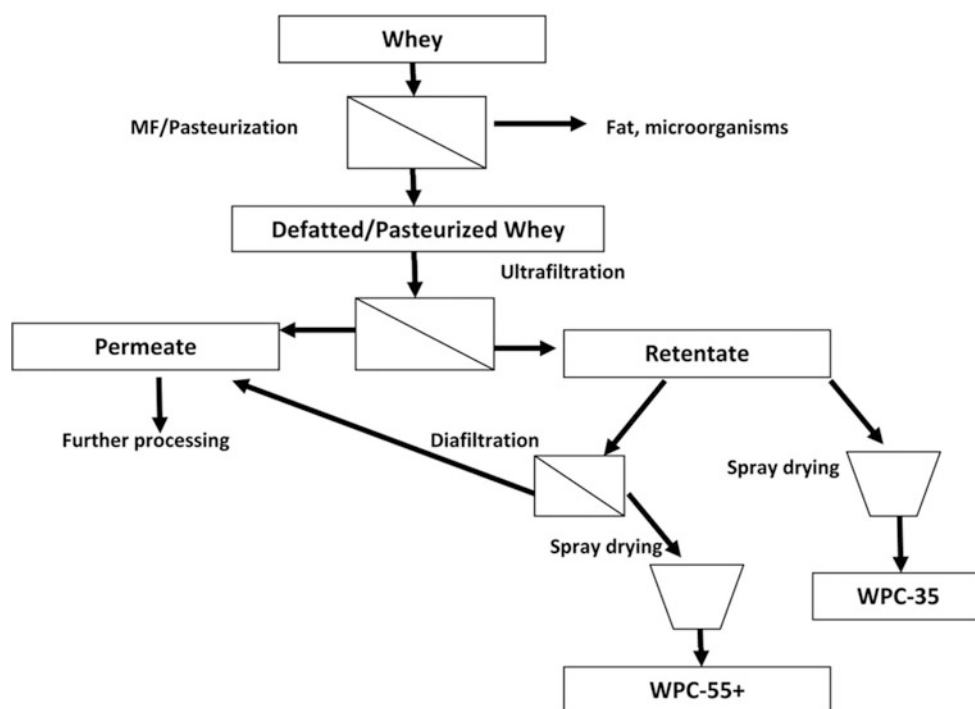
Whey Protein Concentrate: Overview and Membrane Operations, Table 1 Compositional range of commercially available whey protein concentrates and isolates (Foegeding et al. 2011)

Product	Protein (%); DM	Moisture (%)	Lactose (%)	Fat (%)	Ash (%)
WPC-35	34.0–36.4	2.9–4.0	47.0–56.0	2.5–4.0	1.6–8.0
WPC-80	72.9–82.8	3–5.2	0.15–7.4	1–10	2.5–11.0
WPI	90–95	4–6	0.2–2.0	0.2–1.5	0.3–4.5

helix, turn, and extended chains (Considine et al. 2007). The C-terminal region of the molecule is more compact than the N-terminal region, and the different domains show differences in hydrophobicity, net charge, and ligand-binding properties. Among the minor whey proteins, lactoferrin, lactoperoxidase, and immunoglobulins at present have a substantial commercial importance. Lactoferrin (LF) is an 80 kDa iron-binding glycoprotein and consists of about 700 amino acid residues (González-Chávez et al. 2009). In comparison to other whey protein fractions, LF has the highest isoelectric point of 8.0, which means that it carries a positive charge at the physiological pH. It is a simple polypeptide chain folded into two symmetrical lobes (N and C lobes), which are highly homologous with one another (33–41 % homology). LF possesses a greater iron-binding affinity and is the only transferring with the ability to retain this metal over a wide pH range, including extremely acidic pH (González-Chávez et al. 2009). Lactoperoxidase is a heme-containing glycoprotein, containing 608 amino acids with a molecular mass of approximately 78 kDa. The heme group in the active site is covalently bound to the enzyme. The enzyme is stabilized by a calcium ion (Bootsa and Floris 2006). The heme group in the catalytic center of the LP molecule is a protoporphyrin IX, covalently bound to the polypeptide chain through an ester bond. The iron content of LP is 0.07 %, corresponding to one iron per LP molecule. Lactoperoxidase is a basic protein with a high isoelectric point of 9.6 (Seifu et al. 2005). Immunoglobulins (IgGs) are a complex group of proteins comprising IgG, IgA, and IgM. These are major proteins present in the colostrum accounting for 10–15 % of the whey protein and at least 2 % of the total milk protein. Immunoglobulins are glycoproteins and are either monomers or

polymers made up of two light chains (~20–25 kDa) and two heavy chains (~50–70 kDa) linked together with disulfide bonds (Harper 2000).

Whey is a dilute solution of lactose (~5 %) and minerals (~0.6 %), colloidal dispersion of whey proteins (~0.6 %), containing also some lipids and some other several constituents at trace levels (Fox and McSweeney 2003). Considering the composition of concentrated whey protein products (Table 1), it is obvious that substantial amounts of water need to be removed in order to produce products of required properties. For example, the United State Code of Federal Regulations defines whey protein concentrate as “the substance obtained by the removal of sufficient nonprotein constituents from whey so that the finished dry product contains not less than 25 % protein. Whey protein concentrate is produced by separation techniques such as precipitation, filtration, or dialysis. As with whey, whey protein concentrate can be used as a fluid, concentrate, or dry product form. The acidity of whey protein concentrate may be adjusted by the addition of safe and suitable pH-adjusting ingredients.” Depending on the required functional properties, a variety of membrane processes in conjunction with traditional food processing and more sophisticated chromatographic methods can be employed. In general, four membrane technologies are used in whey protein concentration including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). With the realization that the separation of whey into well-defined fractions with specific functionalities would enable optimal use of whey and result in novel product formulations, newer membrane-based processes have been introduced. For example, the electrically driven membrane processes used are electrodialysis and



Whey Protein Concentrate: Overview and Membrane Operations, Fig. 1 Schematic diagram of production of whey protein concentrates

electrodeionization. While the main adsorption technique employed has been ion exchange, with advances in development of new technologies, affinity binding and some other approaches with commercial limitations have been employed. Traditional food processing such as the application of heat may be used at various stages of processing. As a consequence, various whey protein products may have the same protein content but vary in composition of nonprotein compounds, which would in turn impact on their food applications (Fig. 1).

Most commercial WPCs contain either 34–35 or 80 % protein (Table 1). This ingredient is used as a substitute for nonfat dry milk (NFDM) or skim milk powder in the manufacture of yogurt and infant formulae and in various bakery products. WPC-35 is also used in production of stews and sauces due to their thickening behavior in addition to their nutritional benefit. In general, whey is clarified and defatted and thermally treated and then subjected to ultrafiltration. The

resulting permeate mainly consists of lactose and some minerals. The retentate, which now contains almost an equal part of lactose and proteins, may first be further concentrated by evaporation but in many instances is simply spray-dried. The main characteristic and thus performance of this product are based on its composition; high lactose (over 50 %) and mineral contents impact on the behavior of whey proteins in various food applications. Additional removal of lactose and minerals by application of diafiltration results in whey protein concentrates with a greater concentration of proteins. This process basically presents “washing” of nonprotein constituents by diluting retentates by equal amount of water and further ultrafiltration. Depending on the number of diafiltration steps, a range of protein concentrations may be achieved, which would have different industrial application. WPCs containing 80 % protein are usually intended for applications in which proteins play a dominant functional role, such as gelation, emulsification, and foam

formation. Very low lactose content of this WPC makes this product a desirable product for sports nutrition and weight management products.

Further compositional adjustments or manipulations may take place to produce products with required physical properties. For the successful utilization of functional properties of whey proteins in different food systems, they should be recovered in their native, undenatured state and subsequently incorporated in heterogeneous food matrixes. Although chemical and enzymatic modifications of whey proteins are widely applied, they have certain limitations. The application of ultrasound for short duration of time to breakdown protein aggregates formed due to preheating treatments and to prevent reformation of aggregates and the consequent viscosity increase are also in current interest of research (Ashokkumar et al. 2009). In addition, the use of mechanical forces under isothermal and/or isobaric conditions has a significant potential to modify whey proteins (Dissanayake 2011). One of such popular approaches is extrusion, where proteins are thermally denatured under high-pressure conditions technically known as thermoplastic melt. The denatured proteins become fiber form as a result of the process, and sudden release of pressure evaporates water and expands the product. This method has been employed for years and used to produce low-moisture food products such as snacks and breakfast cereals. Another approach termed microparticulation has been used commercially to create whey protein-rich products with enhanced solubility at high temperatures (Dissanayake 2011).

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Whey Protein Fractionation: Overview and Membrane Operations

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Milk is defined as the secretion of the mammary glands of mammals with the primary function to satisfy nutritional requirements of neonates. Milk of some animals, especially cows, buffaloes, goats, and sheep, is used for human consumption, either as such or in the form of a range of dairy products. Milk may also be defined as a true solution of lactose and minerals, colloidal dispersion of milk proteins, and emulsion of milk fat. Fat globules are dispersed into the serum phase of

Whey Protein Fractionation: Overview and Membrane Operations, Table 1 Composition of milk of main mammalian species (Kailasapathy 2008)

Species	Total solids	Fat	Protein	Lactose	Total minerals
Human	12.2	3.8	1.0	7.0	0.2
Cow	12.7	3.7	3.4	4.8	0.7
Buffalo	16.8	7.4	3.8	4.8	0.8
Goat	12.3	4.8	2.9	4.1	0.8
Sheep	19.3	7.4	4.5	4.8	1.0

milk. Milk proteins are grouped into two main classes – caseins and whey proteins, which are obtained by acid or rennet-induced coagulation of casein and their removal from the serum. The milk serum, basically devoid of caseins, is commonly termed the whey. Depending on a source (Table 1), composition of milk and thus the whey varies.

Most serum proteins are globular with relatively high hydrophobicity and compact folding. Most of them have a fairly variable secondary structure with a proportion of α -helix and β -sheet. They readily denature at pH values below 6.5 during heating of milk. The denaturation of these proteins in milk does not result in aggregation but in complex interaction with the casein micelles, changing their chemical and physical properties. The main whey proteins are β -lactoglobulin, α -lactalbumin, bovine serum albumin, immunoglobulins, and some minor proteins including lactoferrin and lactoperoxidase. β -Lactoglobulin is the major serum protein, and due to its proportion in the whey, it tends to dominate the properties of whey protein preparations, especially the heat-induced reactions. Its solubility strongly depends on pH and ionic strength, but it remains soluble upon acidification of milk. Due to its importance, the secondary and tertiary structures of β -lactoglobulin have been well characterized. It has two $-S-S-$ bonds and one free sulfhydryl group, which is buried inside the molecule in the native state. The protein undergoes substantial changes in tertiary and quaternary structure with changes in pH or temperature (Kailasapathy 2008). In milk, it is present as a dimer with a molecular weight of approximately 36 kDa. Both molecules are tightly bound to each other, mainly by hydrophobic interactions which

dissociates at high temperature. Below pH 5.5, β -lactoglobulin associates to form an octamer. At even lower pH values, i.e., below 3.5, the proteins appear as a monomer, which is also the form it takes above pH 7.5. β -Lactoglobulin has a tendency to bind some apolar molecules likely due to its hydrophobicity. α -Lactalbumin acts as coenzyme in the synthesis of lactose. It is a small, compactly folded protein with more or less spherical molecule. It appears as a monomer, stable across wide range of conditions but would start to associate at a higher ionic strength. Bovine or blood serum albumin is a minor protein that gains entrance to milk by leakage from blood serum. It is a large molecule with three globular domains, resulting in an elongated shape. It has 17 disulfide bonds and an unpaired thiol group. Immunoglobulins are antibodies synthesized in response to stimulation by specific antigens. These are large glycoprotein molecules with a heterogeneous composition due to their excretion by different secretory cells. In addition to these proteins found in the milk whey, the whey obtained after production of rennet cheese often contains glycomicropeptide (GMP).

Each of these proteins or group of proteins has been proven or implied to have unique physical or physiological (nutraceuticals) functional properties. Some suggested nutraceutical properties include digestive function (β -lactoglobulin), prevention of caries and induction of satiety (GMP), anticarcinogenicity and sleep enhancement (α -lactalbumin), immunomodulation (lactoferrin, lactoperoxidase), and passive immunity (immunoglobulins). The high content of cysteine in α -lactalbumin appears to improve the immune system, while a high level of tryptophan may help improve mood, sleep, and cognitive performance (Foegeding et al. 2011).

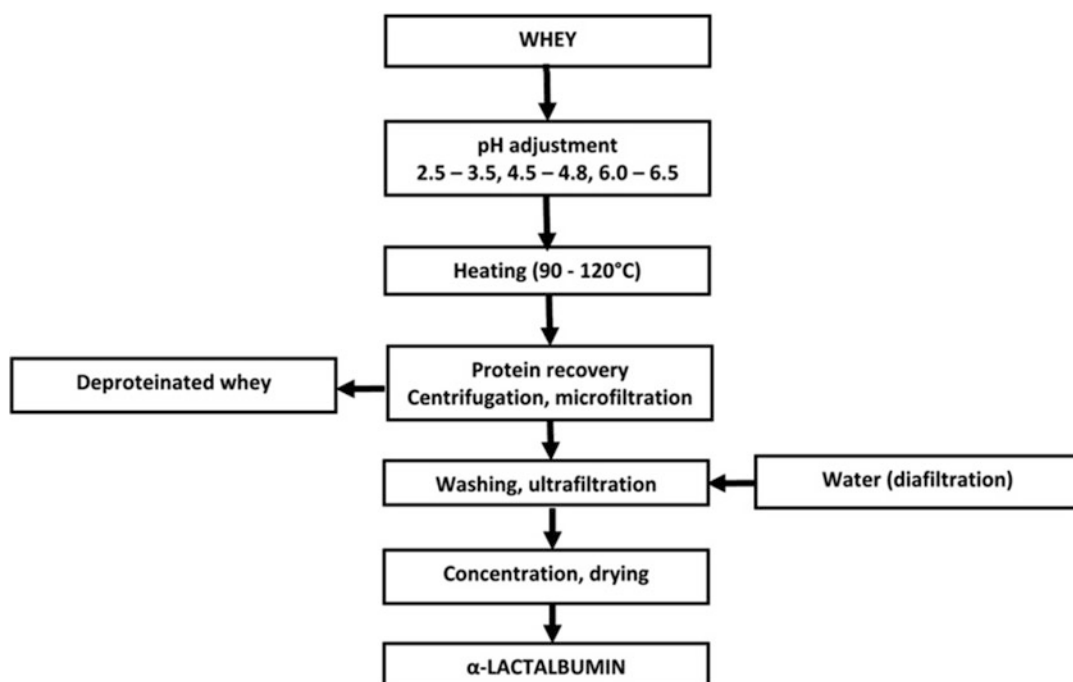
This protein also has a high affinity for minerals, specifically calcium, magnesium, zinc, and cobalt. Through this binding, these minerals are more readily delivered for absorption in the human body. Furthermore, α -lactalbumin is the principal protein of human milk, thus adjusting proportion of the major whey proteins, or completely removing β -lactoglobulin, is a regular practice in manufacturing of infant formulae. GMP, which is a soluble peptide due to attached sugar moiety, *N*-acetylneuraminic acid or commonly known as sialic acid, has various unique characteristics in comparison to other whey proteins. Sialic acid may influence digestive function and promote the growth of probiotics. Suggested applications of GMP include beverage, nutritional bar, dietary supplements, diet foods, and pharmaceutical products (Foegeding et al. 2011). Lactoferrin was originally perceived as an iron-binding protein with antimicrobial properties; however the evidence is mounting showing other important physiological roles including regulation of iron homeostasis, host defense against a broad range of microbial infections, anti-inflammatory activity, regulation of cellular growth and differentiation, and protection against cancer development and metastasis (Seifu et al. 2005). Lactoferrin is used in infant formulae, nutritional foods and supplements, sports nutrition supplements, and pharmaceutical products. Lactoperoxidase (LP) is produced by the secretory epithelial cells and acts as an enzyme and a natural antimicrobial agent. LP is used in nutritional products and personal care products (such as mouthwash, skin creams, and shampoos) (Tamura 2004).

The whey protein products are typical in the sense that they are highly heterogeneous in nature and functionality of these products is combined functionalities of individual fractions. Some of the fractions such as LF and LP are present in such a low concentration which creates additional problems in terms of investment and process establishment. In addition to this, the composition of whey varies largely due to variations in milk composition and different methods of cheese manufacture of cheeses, subsequently carrying this variation into whey protein products. Fractionation of whey proteins into pure/enriched products

enables the unique properties of these novel protein fractions to be realized. The development of advanced and novel processing technologies for fractionation of the whey proteins allows for proper utilization of the large quantities of underutilized whey proteins. Protein fractionation refers to the separation and isolation of individual proteins from a multicomponent mixture of proteins. Commonly used methods for fractionation of proteins are salt, heat, and pH treatments (denaturation properties), electrophoresis, ion exchange, affinity chromatography (ionic nature), dialysis, gel permeation, size-exclusion chromatography (differences in size), and complexation (chemical and enzymatic reactivity).

Proteins contain hydrophilic amino acids on their surface, which interact with water molecules and thus stabilize them in water. Based on the differences in solubility, proteins can be fractionated by selective precipitation using salt, temperature, and pH. When salt concentration of a solution exceeds a critical limit, the water is being displaced from the protein thereby leaving the protein dehydrated, the condition known as salting out. Commonly used salts for salting-out purpose are ammonium sulfate, sodium chloride, and potassium chloride. Generally a two step process is used in the salting out of proteins. Initially salt concentration is adjusted just below the level needed for precipitation. The protein mixture is centrifuged to remove precipitated protein followed by bringing the salt concentration to slightly higher than the level required for precipitating the protein. This further precipitates the protein of interest, leaving the more soluble proteins in solution. The main limitation of this method is that the separated protein is contaminated with large quantities of salt and purification of the precipitate may be costly.

Another method used to fractionate proteins is isoelectric focusing, which uses isoelectric pH (pI) to induce protein precipitation. Taking advantage of differences in pI, the isoelectric focusing separates a mixture of proteins into their individual fractions. Recently Bonnaille and Tomasula (2008) reviewed several methods for isolating the whey proteins using salt, heat, and pH treatments. β -Lactoglobulin, BSA, and α -lactalbumin were



Whey Protein Fractionation: Overview and Membrane Operations, Fig. 1 Fractionation of α -lactalbumin (Mulvihill and Ennis 2003)

fractionated using sodium sulfate at pH 6. Chemicals such as ferric chloride, polyphosphates, and sodium chloride have been also used. In fractionation using heat and pH adjustments, the driving force is thermal stability of the whey proteins under acidic conditions. For example, thermal aggregation and separation of α -lactoalbumin are possible by acidification with super critical carbon dioxide (Bonnaille and Tomasula 2008). Another approach for recovery of α -lactoalbumin has been described by Mulvihill and Ennis (2003). When whey is heated, the whey proteins readily unfold exposing their otherwise buried sulfhydryl and hydrophobic sites, thus inducing protein–protein interactions. The extent of denaturation and aggregation is governed by energy density, pH, and concentration of Ca and on the commercial scale would be also influenced by composition of whey (Fig. 1). α -Lactoalbumin is thus precipitated by centrifugation and may be washed to remove excess of lactose and minerals, all of which may result in a high, up to 90 % of protein, purity. This

method has been improved by incorporation of microfiltration, which replaces centrifugation. Separated α -lactoalbumin is further washed and purified by ultrafiltration.

Another method for protein fractionation is adsorption chromatography, which involves selective adsorption–desorption of protein components on a solid matrix (resin) packed in a column. When a multicomponent mixture of proteins is passed through the column, based on differences in affinity to the solid matrix, some proteins adsorb on the solid matrix while the remaining components pass through the column. Ion-exchange chromatography is the most commonly used technique for protein fractionation and is based on reversible adsorption–desorption of proteins to a solid matrix. The molecules bound to the matrix are eluted using solutions of different ionic strength and/or pH of the buffer. Ion-exchange chromatography has been in use for production of WPI. This process is also used in the production of low-salt and low-fat WPC 80, LF, and LP. With careful selection of resin, α -lactoalbumin and β -lactoglobulin can be

fractioned using ion-exchange principles (Mulvihill and Ennis 2003). Minor whey proteins such as LP and LF are mainly isolated due to growing interest into their physiological functionality. LF and LP are positively charged at neutral pH while all other whey proteins have a negative charge; thus this difference has been used in their fractionation. Similar approach has been used for extraction of immunoglobulins and GMP. Another possible approach is to increase molecular size of these components, namely, GMP, by cross-linking using an enzyme, transglutaminase. In this approach cross-flow microfiltration with ceramic membranes was used to remove cross-linked GMP. Due to cross-linking, the particle size was increased enabling separation of GMP from other whey proteins using a 0.1 μm pore-size membrane at 0.4 bar transmembrane pressure and 55 °C (Tolkach and Kulozik 2005).

Affinity chromatography uses highly selective ligands that have reversible affinity for a particular protein. When a multicomponent mixture of proteins is passed through the column, certain proteins are attached to the ligands while the remaining protein fractions pass directly through the column. The protein bound to the ligand is eluted using a buffer solution which favors desorption from the column. Affinity separation is the most efficient means of separating the individual proteins from a mixture. It is very expensive and is not commonly used for commercial scale separations.

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Whey Protein Isolation: Overview and Membrane Operations

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Fractionation and concentration of whey proteins from whey is one of the more successful industrial applications of ultrafiltration (UF). However, due to flux decline during operation, the practical limit for whey concentration by UF in modern plants is around 24 % total solids, with a protein to total solid ratio limit of ~0.72:1 (Mulvihill and Ennis 2003). Diafiltration is thus employed to achieve a higher protein to total solid ratio, ~0.80:1, with a total solid content of approximately 28 %. However, the efficiency of UF in whey processing is limited by several factors, the most significant of which are concentration polarization and membrane fouling (Rao 2002). Both factors adversely affect permeate flux, which may also be aggravated by protein–protein and membrane–protein interactions (Lipnizki 2005). These impacts however may be minimized by choosing suitable membrane material and configuration as well as

Whey Protein Isolation: Overview and Membrane Operations, Table 1 Representative composition of two different commercial WPis (Foegeding et al. 2011)

Product	β -Lactoglobulin	α -Lactalbumin	GMP	BSA	Ig	LF	LP
WPI-1	43.8	15.2	20.3	1.2	3.4	NR	NR
WPI-2	69.2	14.2	1.6	3.3	2.1	NR	NR

GMP glycomicropeptide, *BSA* bovine serum albumin, *Ig* immunoglobulins, *LF* lactoferrin, *LP* lactoperoxidase, *NR* not reported; all values are in percentages

the appropriate process conditions such as trans-membrane pressure, feed velocity or recirculation rate, temperature, and composition including pretreatment of whey (Cheryan 1998). Opposing charge on the whey proteins and the membrane induces protein–membrane electrostatic attractions initiating protein adsorption on the membrane surface (Lipnizki 2005). This may result in the undesirable protein unfolding, denaturation, and aggregation especially at high-shear operations (Cheryan 1998). The polymeric polysulfone membrane has been the most widely used membrane in whey UF mainly due to its low cost, good thermal stability, and mechanical properties (Brans et al. 2004). The main problem with the use of the hydrophobic polysulfone membrane in the whey processing in comparison to ceramic or hydrophilic polymeric membranes is associated with greater attraction between the membrane surface and the proteins through the hydrophobic and electrostatically induced interactions resulting in severe fouling and flux retardation (Brans et al. 2004). Today ceramic membranes are gaining more attention because of their greater resistance against cleaning and disinfection.

Due to abovementioned limitations, whey protein isolates are manufactured commercially by one of two fundamentally different processes – microfiltration followed by ultrafiltration or ion exchange (Neville et al. 2001). These two processes use completely different methods to isolate the valuable proteins that are present in low concentrations in cheese whey. Microfiltration is a key step during concentration. The pore size of the membrane is selected to capture all the residual fat, particulates (i.e., denatured protein), and microbial debris, while allowing the soluble protein and all

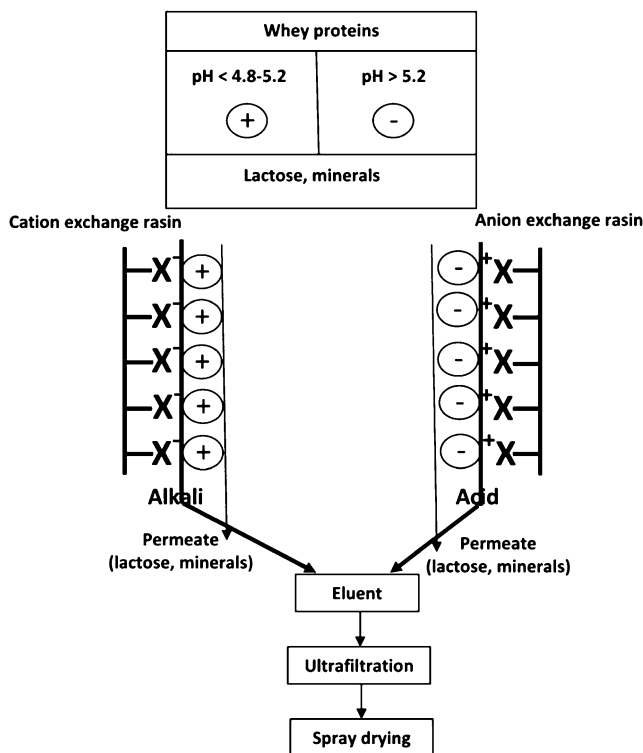
the other components (e.g., lactose, minerals) to pass through unhindered. This prevents membrane fouling in the following steps. The clarified material forms the feed to the second membrane-processing step, ultrafiltration. This process produces a WPI that differs from the ion exchange analogue in that there is no chemical modification of the protein, and the glycomacropeptide, normally released during production of rennet type cheeses, is retained in the product. If no pH adjustment is used and the process is carried out under mild temperatures, the final product is almost completely free of denatured material.

Whey proteins due to their diversity are not defined by a single isoelectric point. The isoelectric point of the major proteins varies from 4.8 to 5.2, while some minor proteins have an alkaline isoelectric point. This means that by adjusting pH, it is possible to first remove minerals and then produce whey protein isolates of different compositions (Table 1). Proteins in general have a positive and a negative charge below and above their isoelectric point. At pH values above their isoelectric point, proteins behave as anions that can be adsorbed on anion exchangers. Therefore, protein molecules are removed from liquid whey through chemical binding to specially developed resins, across which the whey flows. The binding is reversible via pH adjustment, and the protein in the eluted material is subsequently concentrated via ultrafiltration. For example, “Vistec” process uses a cellulose-based exchanger in a stirred tank reactor (Mulvihill and Ennis 2003) (Fig. 1). During this process, whey is acidified to pH <4.6, pumped into the reactor, and stirred to allow adsorption of proteins onto the ion exchanger. Soluble material including lactose and minerals

Whey Protein Isolation: Overview and

Membrane Operations,

Fig. 1 Production of whey protein isolate through ion exchange process (Mulvihill and Ennis 2003)



is removed with water, while proteins remain adsorbed onto the resin. The resin is then resuspended in water followed by pH adjustment to >5.5 , which results in protein separation due to changed charge. The proteins are then separated from the resin by filtration and consequently concentrated by ultrafiltration. Another process, “Spherosil,” uses either cationic Spherosil S or anionic Spherosil QMA ion exchanger for fractionation in a fixed-bed column reactor (Mulvihill and Ennis 2003). Similar to the process above, pH of the whey is adjusted, and it is pumped into the column where the proteins are adsorbed onto the surface, while all other unadsorbed material (lactose) is eluted with water. Under ideal operating conditions, over 85 % of the proteins can be recovered (Mulvihill and Ennis 2003). After elution, the released proteins are concentrated and spray-dried (Fig. 1). Due to their high protein purity and solution clarity, WPIs are extensively used as nutritional supplements in sports and health drinks and in protein-fortified beverages. The high protein content improves WPI physical functionality including water binding, gelling, emulsifying,

and foaming. While obviously composition of WPIs can be manipulated during their production, pH can additionally be altered prior to drying, creating a WPI with an acidic pH, primarily designed for use in acidic beverage applications.

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Whey Ultrafiltration

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History and Application of Ultrafiltration

Ultrafiltration (UF) of whey is common in dairy processing. It was the first membrane application to dairy processing, which commenced in the 1970s upon the development of sanitary membrane modules (Pouliot 2008). The early installations of UF were used to concentrate milk prior to cheese making and in the recovery of whey proteins. In the application for whey protein recovery, UF separates the whey complex by blocking whey proteins by size exclusion, leaving the module via the concentrate. The lactose and mineral-rich solution that is removed via passing the membrane leave the module as permeate. In the early applications of UF, the market for the whey protein concentrate (WPC) was small, so a great effort was devoted to finding applications in food systems in the 1980s. The whey proteins are now commercially valuable and are often sold as a nutritional supplement, particularly for the sport of body building, but also as an ingredient in functional or health-promoting foods (Ramchandran and Vasiljevic 2013).

Function of Ultrafiltration and Operation Modes

The function of the UF to remove whey proteins relies on its molecular weight cutoff (MWCO),

which is defined as the lowest molecular weight solute in which 90 % of the solute is retained by the membrane. The MWCO of UF membranes ranges from 10^3 to 10^6 Da. In terms of physical size, the pore size of UF membranes can vary between 1 nm and 0.5 μm (Pouliot 2008). In general, this means UF membranes are highly effective at blocking colloids, macromolecules, and viruses but passing sugars and minerals. The pressure of UF systems ranges from 3 to 10 bar. In a single stage, UF is capable of concentrating whey by 10–30 times that of the feed. To achieve high protein purities, UF can be applied in diafiltration mode, where a solvent (typically water) is added during UF to “wash out” the components that permeate the membrane (Hausmann et al. 2013a). For example, whey protein concentrate (WPC) of 99 % protein purity can be produced when UF is combined with diafiltration (Henning et al. 2006). An obvious drawback of diafiltration is the large volume of watery waste produced.

UF has greatly assisted dairy processors, providing a low temperature equivalent to the traditional costly thermal processes which would alter the texture of the whey and denature proteins. UF membranes used in dairy processing are typically in spiral wound format. Spiral wound membrane modules involve the flat membrane sheets coiled around a central tube to carry out the permeated fluid, which is key to their low unit cost and success of UF in the dairy industry.

Membrane Fouling and Control Techniques

A key issue in UF of whey is membrane fouling, which has the effect of reducing the flux and permeate production in the installed system. Fouling is a complex effect which combines both the effect of flux, as well as the interaction chemistry between the membrane material and the components of whey (Ramchandran and Vasiljevic 2013). In the effect of flux, the selective depletion of lactose and minerals through the membrane causes a steep rise in concentration of the blocked proteins near the surface. This effect is known as

concentration polarization and causes flow resistance and flux decline. Also, all components in the whey will interact with the membrane where strong adsorption can take place which also causes resistance to flux. The interactions however are very complex, and in studies of whey component interactions on hydrophobic polytetrafluoroethylene, the key components responsible for fouling are the whey proteins and minerals (Hausmann et al. 2013b). The role of proteins and calcium phosphate (a dominant mineral found in whey) in interacting with the membrane and then building up the resistive layer was highlighted in a recent review by Koh et al. (2013).

Concentration polarization and surface adsorption are effects that cannot be avoided, but are managed by choosing important features such as membrane material, operation temperature, applied pressure, and crossflow velocity. Despite these control techniques, the membrane still must be cleaned to remove built-up fouling material as well as to disinfect the membrane. Therefore, a cleaning process is carried out to thoroughly clean the membrane and remove any potential biological contaminants. Cleaning can be performed mechanically, hydraulically, electrically, or chemically (Koh et al. 2013). Chemical cleans are most common and are carried out as part of a routine clean-in-place (CIP). Cleaning can be carried out daily as part of the need to disinfect the membrane processes to prevent biological contamination (Zeman and Zydney 1996). The CIP process requires the membrane plant to be put offline for the cleaning to occur. CIP can be carried out with an alkaline solution, such as sodium hydroxide solution, to remove organic matter such as fats and proteins. An acidic clean is also carried out to remove minerals, particularly those which form scale on the membrane like calcium phosphate. Additives can be included in the CIP, such as surfactant, enzymatic, and chelating compounds, to facilitate cleaning. The choice of which will depend on the specific chemistry of the fouling, for example, enzymatic cleaners can be used to remove proteinaceous fouling. If cleaning cannot restore the membrane flux, or the membrane has been degraded in time leading to lost rejection, the membrane requires replacement. The lifetime of

the membrane in dairy applications depends on the membrane material, operation conditions, and severity of cleaning. Generally, polymer membranes are expected to last 1 year, while ceramic membranes will last 5 years.

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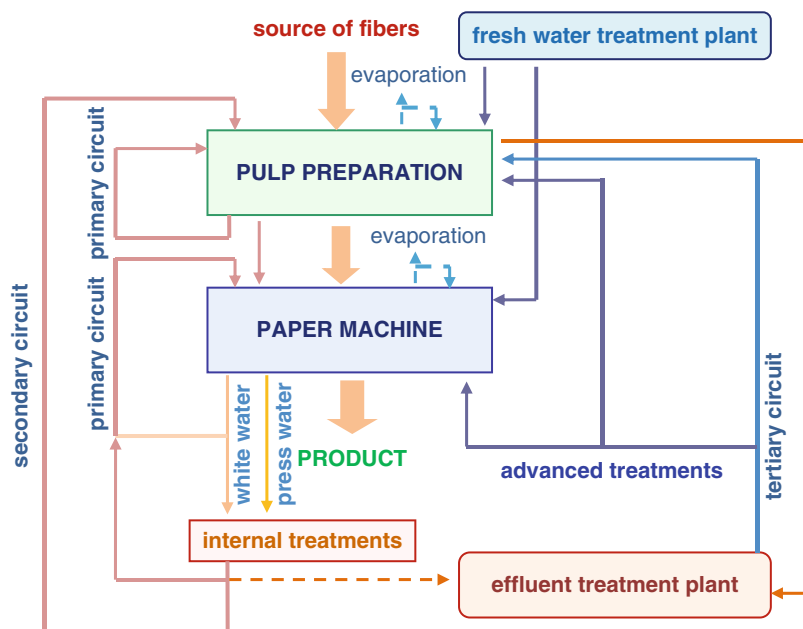
White Water Recovery by Membrane Operations

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The water system of a modern paper mill is divided in several water loops where the water is used in countercurrent. A strict separation of loops

White Water Recovery by Membrane Operations,

Fig. 1 Outline of a paper production process (Adapted from The Handbook of Environmental Chemistry: Emerging Challenges in Wastewater Reuse: Contaminants, Treatment, and Effects Blanco et al. 2015)



is required to minimize transferring detrimental substances from more contaminated to cleaner circuits. In this way, the paper machine, which addresses the highest water quality requirements, is kept as clean as possible to produce a high-quality final product. Thus, fresh water is just mainly used at critical points such as the wire and press section showers or for the preparation of chemicals.

White water loop or paper machine loop holds the highest flow and best quality standards. It can represent more than half of the total effluent load generated in the mill if it is not reused. The main objective of this loop is to dilute the thick stock within the approach system to about a 1 % consistency (10 g/L) to facilitate the mixing of fibers, fillers, and additives in the headbox and their homogeneous distribution on the paper machine wire. In the wire section, a fiber web is formed and dewatering is performed. The retention of solids on the wire is critical for paper quality, whereas water drainage is a key factor for machine speed; both of which can be controlled by the addition of additives. Conditions on the wire section such as retention, dewatering, and additive performance are decisive regarding white water characteristics.

Later on, in the press section, formed by several press nips, the paper sheet is consolidated, and the dry content of the paper web is increased as much as possible by compression (up to approximately a 40–55 % consistency depending on the product to produce and the raw material and machine that are used) (Holik 2006). Dewatering of felts is performed by suction pipes.

The dewatering water from the wire and press sections is called white water. It is collected, clarified (to recover solids), and reused in the white water's loop. The excess of water is sent in countercurrent to the previous water loop.

Thus, white water is intensively recirculated through the process to minimize water consumption. It is firstly reused in the paper machine primary circuit, which consists in a short loop with the main purpose of diluting the stock within the approach system (Fig. 1). The white water that is drained from the paper machine is firstly clarified in save-alls, mainly by filtration, or other water treatment technologies such as dissolved air flotation. Disk filters are the prime technology used in save-alls, which shows the advantage of being able to produce different water qualities, namely, cloudy, clear, and super clear, corresponding to

their solids content. Furthermore, trouble associated to fouling and energy consumption may be of less importance when implementing membrane technologies. In mills producing high-quality grades with closed water circuits, the BREF (2013) recommends an advanced white water treatment. Membrane processes obtain water of different qualities according to the needs of each process, including high qualities, as required for pressure showers, the preparation and dilution of chemicals, vacuum systems, and sealing water for pumps and agitators (Nuortila-Jokinen et al. 2004; Judd and Jefferson 2005; Kallioinen et al. 2010; BREF 2013).

Different ultrafiltration systems have been implemented to improve the quality of the white water that is reused in the paper machine, such as in Metsä-Serla Kirknemi mills in Finland, Stora Enso mills in Kabel and Utersen, Germany (Nuortila-Jokinen 2003), and PM61 Holmen Paper Madrid (Monte et al. 2011). Besides the need of reducing water consumption, the use of ultrafiltration has been addressed to keep the paper machine cleaner by improving process water quality (removal of solids and microorganisms), to reduce the number of breaks, and to minimize cleaning maintenance (Nuortila-Jokinen 2003; Monte et al. 2011). On the other hand, to further improve internal water use, white water may be recirculated in a secondary circuit, where internal kidneys based also on membrane technologies, biological treatment, evaporation, or ozonation processes, among others, may be implemented.

The performance of membrane systems within paper mills is fully affected by fouling and erosion of the active layer (Monte et al. 2011) because white water usually carries a high amount of suspended solids (mainly fibers), colloidal and dissolved organic matter, and inorganic compounds such as calcium carbonate and silica. The influence of process parameters on water quality is a critical issue to consider in the implementation of membrane systems. Particularly, the performance of the retention system and the use of additives (biocides, cationic compounds, and sizing agents, among others) must be controlled and evaluated during membrane operations as

they significantly affect the characteristics of the resulting white water. Moreover, the level of circuit closure, which is directly related to the contamination level of process water, must remain at a level that may be tolerated to keep the quality of the produced paper and the runnability of both the paper machine and the associated water treatment technologies.

Although microfiltration might have been expected to allow better fluxes for white water treatment than ultrafiltration, these systems could show similar performance problems than ultrafiltration because the foulants that are associated to this type of water (such as bacteria, pitch, and stickies) are of a very similar size to the pores of microfiltration membranes (Hubbe 2007; Kaya et al. 2010).

The treatment of white water by reverse osmosis or nanofiltration systems may produce water of enough quality to be used in the most critical points of the paper machine, such as high-pressure showers; but their use is limited because of the membrane fouling caused by organic and inorganic compounds (mainly calcium carbonate and silica) even when an appropriate pretreatment such as ultrafiltration is complementarily implemented (Kaya et al. 2010; Ordoñez et al. 2010).

Some important general issues considering the use of membranes for white water recovery are any type of membrane filtration cannot handle sudden peaks of suspended solids; high-pressure filtration methods produce cleaner water, but consume more electricity and must be sized larger or equipped with more efficient pretreatment or countermeasures to protect against plugging; pretreatment processes such as chemical coagulation, adsorption, sedimentation, or flotation may be required to reduce the associated problems to membrane fouling (Hubbe 2007); symmetric membranes have a higher tendency to plug, although plugging may be avoided by maintaining highly turbulent conditions, which otherwise will require more energy; and final treatment and disposal of the concentrates must be considered (BREF 2013).

The current tendency to make membrane systems competitive for the treatment of white water

is to develop low fouling membrane processes, such as those systems with higher associated cross flow velocities (e.g. rotation systems) (Monte et al. 2011), or better membrane materials. Characteristics such as hydrophilicity, pore size, surface roughness, and retention capacity have a very important effect on the development of membranes to be used for this application (Kaya et al. 2010).

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Wide-Angle X-Ray Diffraction (WAXD)

► Wide-Angle X-Ray Scattering (WAXS)

Wide-Angle X-Ray Diffraction Pattern

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According to the Wide-Angle X-ray Diffraction (WAXD) method, the sample is scanned in a wide-angle X-ray goniometer, and the scattering intensity is plotted as a function of the 2θ angle.

When X-rays are directed in solids, they will scatter in predictable patterns based upon the internal structure of the solid. A crystalline solid consists of regularly spaced atoms (electrons) that can be described by imaginary planes. The distance between these planes is called the d-spacing. The intensity of the d-space pattern is directly proportional to the number of electrons (atoms) that are found in the imaginary planes (Warren 1990).

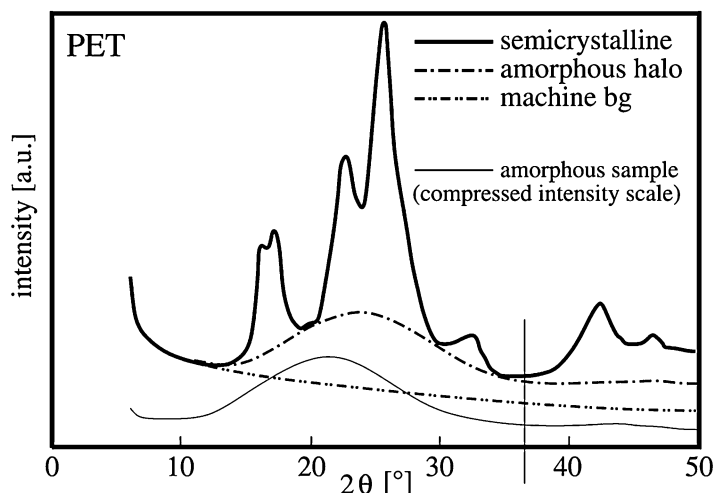
Every crystalline solid will have a unique pattern of d-spacings, which represents a *fingerprint* for that solid. In fact, solids with the same chemical composition but different phases can be identified by their pattern of d-spacings.

For semicrystalline isotropic materials, a qualitative measure of crystallinity is directly obtained from the respective WAXD curve.

Figure 1 shows the phenomenon for poly(ethylene terephthalate) (PET) membrane (Stribeck 2007). The curve in bold solid line shows a WAXD curve with many reflections. The material is a PET with a high degree of crystallinity. The thin solid line at the bottom shows a compressed image of the corresponding scattering curve from a completely amorphous sample. Compared to the semicrystalline material it only shows two very broad peaks – the so-called first and second order of the amorphous halo.

Wide-Angle X-Ray Diffraction Pattern,

Fig. 1 WAXD curves from semicrystalline and amorphous poly(ethylene terephthalate) (PET). Separation of the observed intensity into crystalline, amorphous, and machine background (laboratory goniometer Philips PW 1078, symmetrical-reflection geometry) (This figure has been taken from Stribeck (2007) (Fig. 8.2, p. 102))



It is obvious that the semicrystalline material contains this amorphous feature as well, underneath the reflections. In the semicrystalline material, the halo is shifted to higher scattering angle. In fact, the dash-dotted curve is simply an image of the scattering curve of the amorphous material stretched in the vertical as well as in the horizontal direction.

The dash-dot-dotted curve shows the *instrumental background* of the goniometer. Identification of the observed peaks can be accomplished by means of data listed in the *Polymer Handbook* (Brandrup et al. 2005).

A simple method can be used to describe changing crystallinity from WAXD data of isotropic materials. It is based on the computation of areas in Fig. 1. At first, the border between first-order and second-order amorphous halo is identified. For PET, this is at $2\theta \approx 37^\circ$ (vertical line in the plot). Then the area, A_{am} , between the amorphous halo and the machine background is integrated. Finally the area, A_{cr} , between the crystalline reflections and the amorphous halo is integrated and the crystallinity index X_c , $X_c = A_{cr}/(A_{am} + A_{cr})$, is computed.

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Wide-Angle X-Ray Scattering (WAXS)

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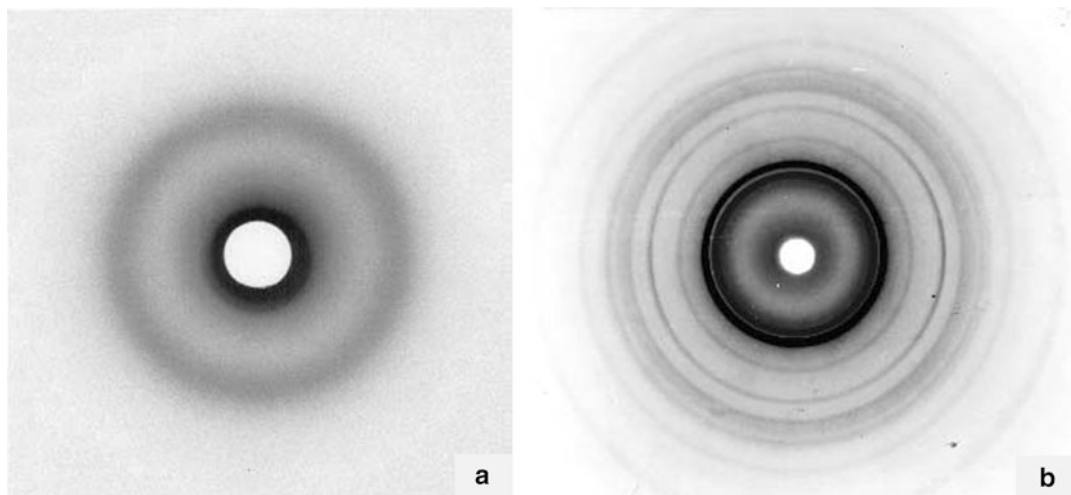
Synonyms

Wide-Angle X-ray diffraction (WAXD)

Wide-Angle X-ray Scattering (WAXS) or Wide-Angle X-ray Diffraction (WAXD) is an x-ray-diffraction technique that is often used to determine the crystalline structure of inorganic and organic polymeric membranes. This technique specifically refers to the analysis of Bragg peaks scattered to wide angles ($2\theta > 1^\circ$), which by Bragg's law implies that they are caused by subnanometer-sized structures.

The Debye's equation (Guinier 1963)

$$I(q) = \sum_{i,j}^N f_i f_j \frac{\sin(qr_{ij})}{qr_{ij}} e^{-2\sigma_{ij}^2 q^2}$$



Wide-Angle X-Ray Scattering (WAXS), Fig. 1 Wide-angle X-ray scattering from (a) polystyrene, showing a diffuse halo from an amorphous sample; and (b) highly

crystalline polyethylene, showing sharp ‘powder’ rings (This figure has been taken from Bower (2002), Fig. 3.9, p. 81)

provides a relationship between interatomic distances r_{ij} and the x-ray scattering factors f_i and f_j of the atoms i and j respectively.

$$q = 4\pi \frac{\sin(\theta)}{\lambda}$$

represents the scattering vector and $e^{-2\sigma_{ij}^2 q^2}$ is the Debye–Waller thermal factor.

σ_{ij}^2 is the atomic mean-square displacement. Thermal motion reduces WAXS intensity.

To derive the equation, it is assumed that the sample is composed of perfect crystals of finite dimensions randomly oriented, each consisting of N atoms that vibrate with harmonic motion. Wider is the motion, greater is the Debye–Waller factor.

The Fourier transform of the reduced intensity $I(q)$ results in a radial distribution and hence provides information about short and medium range order in the sample.

Wide-Angle X-ray Scattering is the same technique as Small-Angle X-ray Scattering (SAXS); only the distance from sample to the detector is shorter and thus diffraction maxima at larger angles are observed. Depending on the measurement instrument used, it is possible to do WAXS

and SAXS in a single run (Small- and Wide-Angle X-ray Scattering SWAXS).

At third generation synchrotron radiation sources, the development of μ -sized beams allows to perform time-resolved μ SAXS/ μ WAXS experiments on polymeric membranes during melting, crystallization, and deformation aiming to visualize and understand the evolution of nanostructures (Stribeck 2007; Nozue et al. 2007).

Amorphous structures yield scattering halos (broad peaks) whereas crystalline structures are characterized by Bragg peaks (Fig. 1). WAXS is therefore a good monitor of crystallinity in the sample.

This technique is a time-honored but a somewhat out-of-favor technique for the determination of degree of crystallinity of inorganic and/or organic membrane polymeric samples. The diffraction pattern generated allows to determine the chemical composition or phase composition of the membrane film, the texture of the membrane film (preferred alignment of crystallites), the crystallite size, and presence of film stress.

According to this method, the sample is scanned in a wide-angle x-ray goniometer and the scattering intensity is plotted as a function of the 2θ angle.

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Wine Aroma Enhancement

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Aroma-A primary wine aroma refers generally to a pleasant smell of fruity, floral, herbal, mineral, and/or woody flavors of young wine, unique to each grape variety, which will be interpreted by the olfactory bulb. Secondary wine aromas are those flavors that arise from the chemical reactions during fermentation and aging in barrels, while tertiary aromas are those smells that are developed by aging in the bottle. The term bouquet generally refers to both secondary and tertiary aromas, while the term odor is related to an unpleasant smell due to possible wine faults.

The typical aroma of wines is mainly due to volatile compounds that come from the grape. Apart from free flavor compounds, a significant part of several aroma compounds is accumulated in the grape berry as odorless nonvolatile glycosides. Odorous volatiles come available after acid or enzymatic hydrolysis from glycosides during wine storage, arise after aging on lees or micro-oxygenation, and can be enhanced by membrane technology.

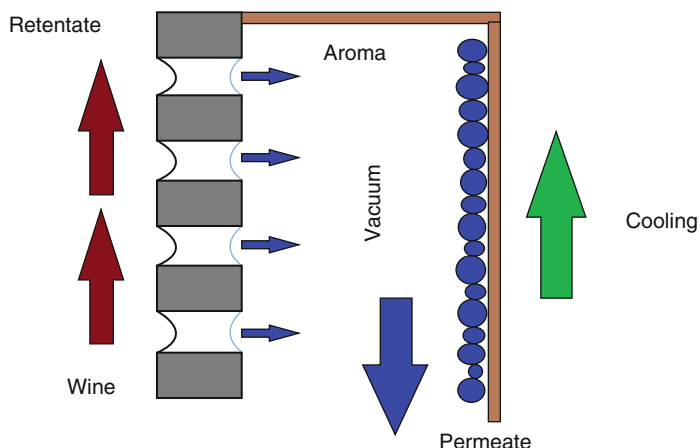
The glycosylated aroma fractions that can give rise to odor-active compounds upon

hydrolysis include monoterpenes (e.g., linalool, nerol, geraniol, α -terpineol, and citronellol), benzenoid compounds (e.g., phenol, guaiacol, 4-vinylguaiacol, and 4-vinylphenol), norisoprenoids (e.g., damascone, 3-hydroxy damascone, and enyne diol), and aliphatic alcohols (e.g. 3-methylbutanol). Acid hydrolysis occurs quite slowly in winemaking conditions. Moreover, exogenous glycosidases (β -glucosidase, α -rhamnosidase, α -arabinosidase, and β -apiosidase) from yeast and filamentous fungi may be used for enzymatic hydrolysis of mono- and diglycosides to enhance wine aroma (Cabaroğlu et al. 2003). Wine aroma quality may be further improved by micro-oxygenation with increase of some aroma attributes (plum, currant, spicy, and liquorice) and decrease of herbaceous aroma (Cejudo-Bastante et al. 2011), while aging on lees changes aroma balance by binding volatile compounds, such as lactones, terpenoids, ketones, aldehydes, and esters (Liberatore et al. 2010).

Membrane distillation is a relatively novel membrane process, which can be applied for the recovery of aroma compounds (Gryta 2005). Dense hydrophobic membranes with pores filled by gas phase are used in this process. The hydrophobic nature of the membrane prevents penetration of the wine into the pores. Therefore, only volatile components of the wine may be transported through the membrane. The concentration gradient of some particular volatile species in the gas phase at both ends of the membrane pores causes their transport across the membrane. The composition of the gas phase above the liquid surface is often expressed by the partial pressure, and thus the partial pressure difference can be used as a driving force of the membrane distillation process. The value of this driving force depends upon the temperature and composition in the layers adjacent to the membrane surface. When the driving force is obtained by partial pressure reduction on the permeate side by applying vacuum or blowing a sweep inert gas on this side, the membrane separation process is called pervaporation (Fig. 1). Usually the pressure of the permeant components is lower than their saturation pressure, and these components are therefore removed as vapor. Permeate should be collected

Wine Aroma Enhancement,

Fig. 1 Aroma recovery by pervaporation



in traps, which are normally cooled by using cold water or liquid nitrogen.

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Wine Aroma Enhancement, Membrane Operations of

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Wine aroma enhancement – The aroma profile of wine is made up by a subtle ratio between compounds of widely varying sensory properties.

During wine making, several components are lost due to their high volatility in aqueous solutions. These compounds are rather important for the sensorial quality of wines and might therefore be recovered and added back to the wines. Complete aroma recovery before dealcoholization and adding back to dealcoholized wine is another application (Catarino and Mendes 2011). Pervaporation, osmotic distillation or evaporative perstraction, reversed osmosis, and nanofiltration may constitute promising membrane processes for recovering aroma compounds from wines.

Pervaporation – This separation process is based on selective transport inside a dense hydrophobic membrane associated with the evaporation of the permeant. Aroma compounds permeate through the membrane due to the vacuum on the downstream side of the membrane. Once the aroma compounds leave the membrane as vapor, they will be condensed and collected under cryogenic temperature. Poly-octyl-methyl-siloxane/polyetherimide composite asymmetric membrane or poly-dimethyl-siloxane flat sheet or spiral wound membranes may be used for the aroma recovery from wine by pervaporation.

Osmotic distillation or evaporative perstraction – This process involves the use of a microporous hydrophobic membrane to separate two circulating aqueous solutions at different solute concentrations. The wine phase containing the volatile components circulates through a hollow fiber membrane contactor, while the stripping

Wine Aroma Enhancement, Membrane Operations of, Table 1 Solute rejection by RO and NF membranes (Labanda et al. 2009)

Compound	Osmonics – SE	Rejection (%)	
		Toray – UB70	Osmonics – DK
Diethyl succinate	99	96	97
2-Phenyl-ethanol	97	95	95
cis-3-Hexenol	80	77	85
Isovaleric acid	86	76	65

liquid, e.g., degassed water, flows along the downstream side of the membrane. When operating pressure is kept below the capillary penetration pressure of liquid into the pores, the membrane is not wetted by the circulating solutions, and air gaps are formed within the pores of the membrane. Process will be performed at room temperature, causing no thermal degradation of volatile compounds. Solubility of wine aroma compounds is higher in the wine phase than in pure water, so their transfer into the stripping phase is limited. On the other hand, ethanol is preferentially transferred across the membrane pores into the stripping phase due to the vapor pressure gradient between the feed and stripping phase (Diban et al. 2008).

Nanofiltration and reversed osmosis – Concentration of specific aroma compounds such as diethyl succinate (wine aging), 2-phenyl-ethanol (floral note), cis-3-hexenol (herbaceous note), and isovaleric acid (undesired note) of model white wine can be achieved by reversed osmosis and nanofiltration using flat sheet polymeric membranes in a batch retentate-recycling mode. High solute rejection values indicate enhanced aroma concentration in the retentate stream phase (Table 1) (Labanda et al. 2009).

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Wine Clarification by Membrane Operations

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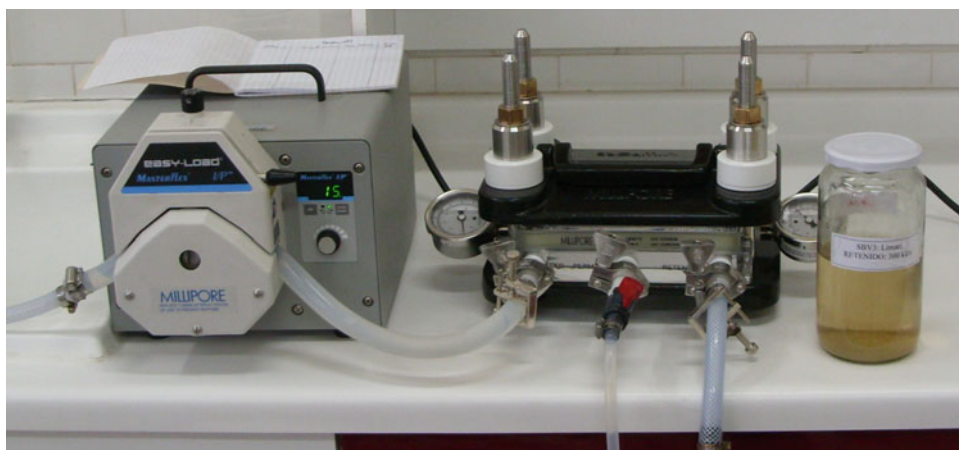
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Wine Clarification

Wine turbidity is caused by suspended material like yeast residues and macromolecular compounds with colloidal behavior. The clarification operation to remove this material is traditionally performed by diatomaceous earth filtration and membrane operations have been relatively restricted because of possible removal of polysaccharides and other macromolecules that may be of major relevance to wine quality.

Cross-Flow Microfiltration

This more recent operation uses a selective porous membrane that filters a wine in order to achieve its purification or clarification, resulting into a clear appearance and making the wine microbiologically stable. By creating a turbulent stream on the surface of the membrane, settling of filtered particles on the membrane will be prevented. Two



Wine Clarification by Membrane Operations, Fig. 1 Cross-flow ultrafiltration of white wine

main types of membranes are currently available: organic membranes made from polymeric material and inorganic membranes made from ceramics. Hollow fiber membrane systems are generally preferred. This membrane geometry is very compact, which means that a large filtration area per unit of volume will be available. Moreover, it does not require a large recirculation flow rate, giving less mixing and heating of the wine.

Process Integration

This relatively new concept involves the coupling of two or more unit operations that provide a more efficient separation than each operation alone. The integration of adsorption and cross-flow microfiltration may reduce unstable protein concentration in white wine, increasing at the same time the permeate flux of microfiltration due to less severe membrane fouling. After adsorption using a packed column of zirconium oxide pellets and cross-flow microfiltration using a ceramic membrane of zirconium oxide with a pore size of 0.2 μm , an increase of 15–20 % of the permeate flux has been observed. About 47 % of the total protein concentration and 15 % of the total polyphenol concentration have been lost during the adsorption stage. Only the percentage of total, volatile, and fixed acidity of wine decreased after using the hybrid process without changing the

other physicochemical wine properties (Salazar et al. 2007).

Cross-Flow Ultrafiltration

This membrane operation may be a good alternative for white wine clarification instead of cross-flow microfiltration in terms of productivity, wine quality, and tartaric stability (Fig. 1). Use of polymeric ultrafiltration membranes with a molecular weight cut-off of 100 kDa proved to have similar clarification performance for white wine as polymeric microfiltration membranes with 1.0 μm pore size. Polysaccharide removal was low with both microfiltration and ultrafiltration membranes. Wine polysaccharides may act as precipitation inhibitors of potassium hydrogen tartrate crystallization and their removal may decrease tartaric stability of wine (Gonçalves et al. 2001).

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Wine Clarification by Microfiltration

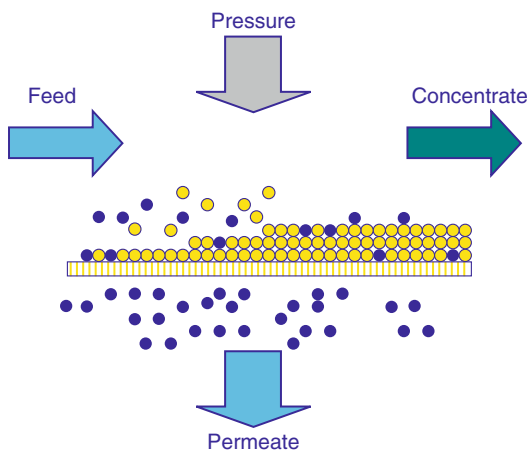
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Wine clarification – Crude wine is a complex medium with a turbid aspect. This latter is not well accepted by the consumer, and wine needs to be clarified removing particles such as microorganisms (yeast and bacteria), cell debris, colloidal aggregates (tannin, pectin, and mannoprotein), and potassium tartrate crystals by microfiltration. Thus, the key roles of clarification are to provide limpidity and microbiological stabilization of wines.

Microfiltration – Cross-flow microfiltration could be an alternative for traditional solid–liquid separation technologies such as centrifugation, filtration on sheets, diatomaceous earth filtration, and the use of exogenous additives during wine making. It offers several advantages such as no health and environmental problems because of the elimination of diatomaceous earth use, as well as the combination of clarification, stabilization, and sterile filtration in one single continuous unit operation without significantly modifying sensory quality of wines. The wine to be filtered flows parallel to the membrane surface and solutes and salts pass through the membrane by mean of a pressure drop. The shear exerted by the feed solution flowing parallel to the membrane surface may sweep deposited particles toward the retentate side, and so the deposited layer of particles and colloids remains relatively thin (Fig. 1).

The correct choice of operating conditions and membrane plays a key role to minimize membrane fouling. Microfiltration performance is governed by colloids and small particles, where these constituents result into a sharp initial flux decline related to both internal and external fouling. Therefore wine filtration should be done below critical flux above which an irreversible deposit appears at the membrane surface. Applied pressure should be smaller than the critical



Wine Clarification by Microfiltration, Fig. 1 Cross-flow microfiltration

pressure, where the particles brought to the membrane surface by the permeate flow are transported back into the bulk suspension by diffusion and flow out of the membrane. Transmembrane pressure is generally in the range between 1 and 3 bars. Moreover, cross-flow velocity affects mass transport of particles nearby membrane surface by increasing shear stress and shear induced diffusion. A cross-flow velocity of 2 m/s is usually applied, which insures sufficient shear stress and preserves wine quality. A major problem of increasing cross-flow velocity is the rise of wine temperature. Temperature should not exceed 25 °C in order to not modify sensorial characteristics of wine. Furthermore, organic membranes of cellulose acetate, polypropylene, polyethersulfone, and polyvinylidene difluoride and ceramic membranes of zirconium oxide, alumina, and titanium oxide with an average pore diameter of 0.2 µm for red wines and 0.1–0.22 µm for white wines show fair results in terms of permeate flux and wine quality (El Rayess et al. 2011).

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X-Ray Diffraction (XRD)

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X-ray diffraction occurs when an electromagnetic wave of wavelength of the order of magnitude of 1 Å interacts with an ordered array of atoms like a molecular or ionic crystal. When the electromagnetic wave interacts with the electrons of an atom, a secondary wave (of the same wavelength) is scattered in all directions by the atom itself. The secondary waves produced by the three-dimensional regular array of atoms give rise to interference phenomena which can be destructive or constructive depending on the relative disposition of the atoms. Constructive interference results in diffracted rays scattered only along well-defined directions. The directions and the intensities of the diffracted rays depend on the crystal symmetry and on the atomic number and spatial distribution of the atoms inside the crystal and the set of diffracted rays, thus containing information about the three-dimensional atomic structure of the crystal.

Following Bragg's description of X-ray diffraction, we can assume a crystal as made of infinite planes containing atoms and whose orientations are dependent from the crystal unit

cell parameters. Each family of planes will then diffract according to Bragg's law (Warren 1990):

$$n\lambda = 2d\sin\theta$$

where n is the “order” of the plane, λ is the wavelength of the X-ray, d is the distance between the planes of the family, and θ is the angle between the wave and the plane. Furthermore, a complex but well-defined mathematical relation links the diffracted waves directions and intensities with the electron density inside the diffracting object (Warren 1990).

Therefore, due to their relationship with the spatial arrangements of the atoms inside a periodic structure, the acquisition of the diffracted rays from a material having an internal atomic periodicity (from 1D to 3D) may give important insights into the atomic structure of the material itself.

Experimentally, an X-ray diffraction experiment depends on the physical state of the matter: crystalline (single crystal or polycrystalline), an ordered surface (2D periodicity only), or even with an order in one dimension only like in fibers. In any case the experiments require three essential parts: an X-ray source which is in general monochromatic (conventional sources or synchrotron), a goniometer which is used to orient the sample according to the Bragg's law, and a detector which may be mono- or bidimensional and is used to collect the diffracted rays from the sample (Roe 2000).

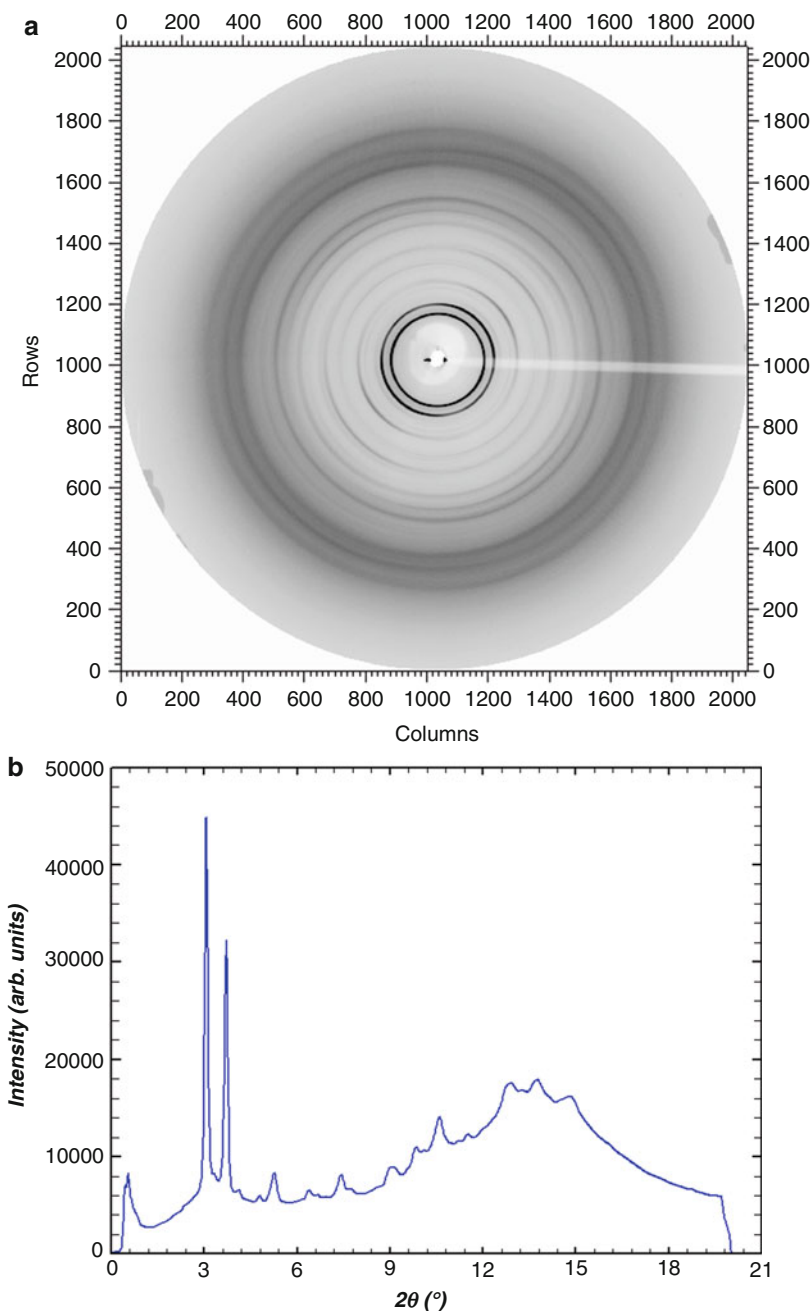
X-ray diffraction is a well-established technique in membranes science (Bower 2002), mostly used for structural characterization but also for the analysis of physical processes occurring at membrane interfaces.

X-ray diffraction has been the main technique for the determination of crystalline polymers

structure. From the diffraction pattern of well-aligned polymer crystallites, it is possible to obtain the unit cell parameters, by inspecting the diffraction pattern geometry and intensities. A more quantitative study, normally carried out on polycrystalline samples (powder diffraction, Fig. 1), may lead to the structural determination

X-Ray Diffraction (XRD),

Fig. 1 (a) 2D powder diffraction pattern of a copolymer based on alternate benzothiadiazole and dioctylfluorene moieties and (b) its integrated pattern (Courtesy of Drs W. Porzio and L. Barba)



of the unit cell content, thus giving a molecular model of the crystalline polymer. Besides, polymer crystal diffraction patterns generally do not contain the full information needed for a complete crystal structure determination, and a modeling procedure is employed by exploiting crystal packing hypothesis based on polymer physics knowledge. The final accepted model is the one which best reproduces the experimental diffraction pattern.

X-ray diffraction is also used in polymer chemistry to estimate the crystallinity index, by evaluating the different contributions to the total diffracted intensity of the amorphous and crystalline components of the sample.

Finally, if one or more of the components of the membrane are in the crystalline state, the analysis of the membrane diffraction pattern may give important insights into the material modification upon membrane preparation.

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X-Ray Synchrotron

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Synchrotron radiation (SR) is produced when charged particles moving at relativistic speed are forced to change their trajectory by a magnetic field. Those particles, typically electrons, loose energy under the form of electromagnetic radiation, and due to their relativistic speed, the emitted radiation is confined in a narrow cone along the direction of the electron's motion (Fig. 1), with a continuous energy spectrum ranging from far infrared to X-ray regions.

In a synchrotron, bunches of electrons circulate in a closed orbit and the electrons are forced to change their directions by magnets, producing intense SR beams tangentially to the magnets themselves. The radiation thus produced is extremely intense and collimated in a narrow vertical angle and can deliver to the sample huge amounts of X-ray photons, several order of magnitude more than conventional laboratory sources (Duke 2008).

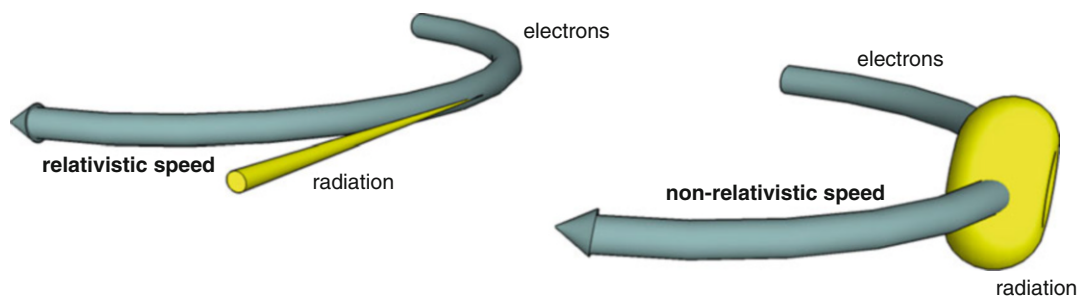
Nowadays, dedicated synchrotrons are built in order to produce extremely brilliant (intense and collimated) X-ray beams, whose properties depend on the synchrotron construction parameters. Apart from intensity and collimation, SR possesses other interesting properties: a continuous spectrum, a high degree of polarization, and a well-defined time structure. All of these properties can be properly tuned for specific X-ray experiments. Apart from bending magnets, which keep the electrons in a closed path, other magnetic devices called *insertion devices* (*wigglers* and *undulators*) are inserted in the straight sections of modern storage rings and can produce even more intense and collimated X-ray beams (Fig. 2).

SR is conveyed into a pipe, the beamline, where it is optically modified in terms of wavelength selection, focusing properties and final beam size. It is finally delivered to the sample, according to the kind of experiment (Margaritondo 2002).

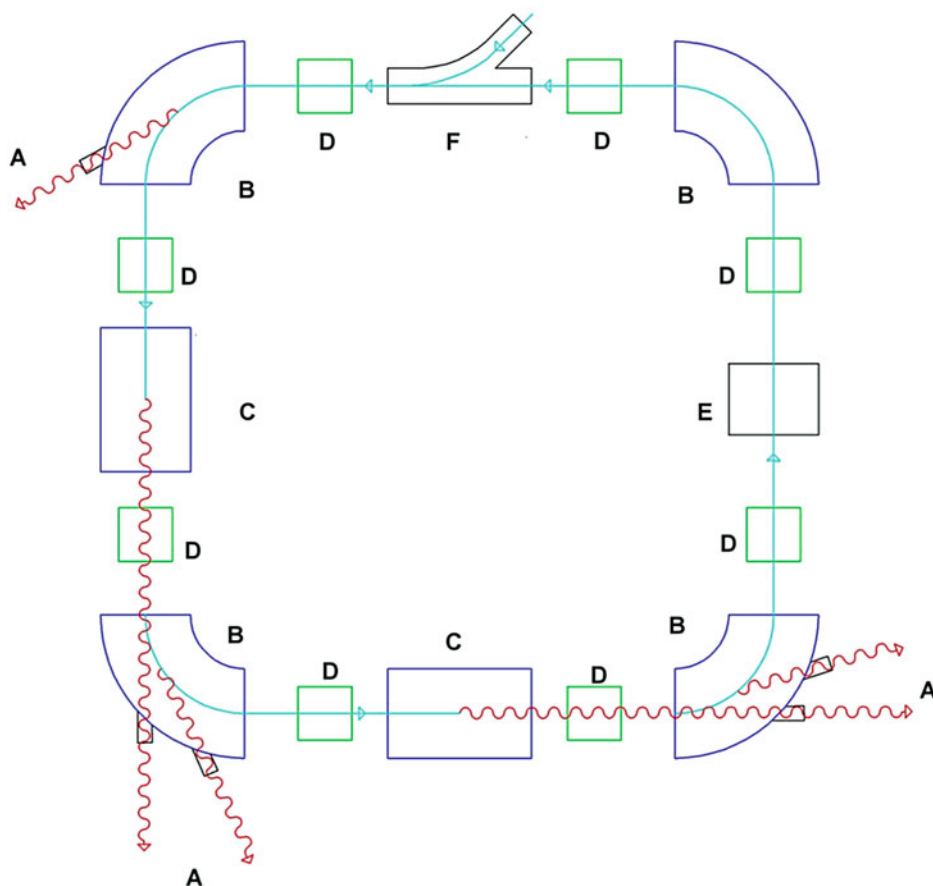
Synchrotrons are generally built for specific SR wavelengths with specific machine characteristics. Lower-energy X-ray beams normally indicated as “soft X-rays” have energies roughly in the range 100–1,000 eV (≈ 10 –1 nm), whereas “hard X-rays” are in the range of 10–100 keV (≈ 0.1 –0.01 nm).

The X-rays produced by synchrotrons have very attractive characteristics for the materials science researcher, which can exploit not only the high photon flux of the SR but also the high collimation of the beam.

Highly brilliant X-ray beam with a size of few μm to few hundreds of nm has been produced and used for microdiffraction experiments. With such a small beam section, the scanning of a single polymeric fiber was possible pinpointing to



X-Ray Synchrotron, Fig. 1 Simplified representation of the angular distribution of emitted radiation from electrons moving at relativistic and nonrelativistic speed and traveling in a circular path



X-Ray Synchrotron, Fig. 2 Sketch of a modern SR-dedicated storage ring. (A) Emitted synchrotron radiation; (B) bending magnets; (C) insertion devices (wigglers,

undulators); (D) quadrupole magnets; (E) radio-frequency cavity; (F) injection magnet. Electron path is represented in magenta

domain inhomogeneities in both size and orientations (Riekel and Davies 2004). The same micro-beam approach was also applied to SAXS and WAXS techniques.

Highly intense and extremely collimated SR beams have also been largely used in SAXS experiments, to provide structural information on the nm size of polymeric and biological

membranes (like lipid bilayers). Soft matter, like biological membranes, is well known as low X-ray scattering material, and the intense SR beam is a unique tool for SAXS studies. Moreover, the strong collimation of the beam allows a resolution impossible to be reached with conventional sources. Wavelength tunability is another characteristic of SR largely exploited in SAXS, where time structure of SR has been used in time-resolved experiments (Chu and Hsueh 2001).

X-ray-based imaging techniques applied to hard and soft matter gained a great benefit from the use of intense and small X-ray beam as for tomographic methods. X-ray photoelectron spectroscopy methods also received a great impulse from the use of X-ray synchrotron radiation. Chemical analysis with photoelectron spectroscopy requires tunable and brilliant SR beams in order to chemically and electronically characterize surfaces like metal-based membranes.

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X-Ray Synchrotron Microtomography

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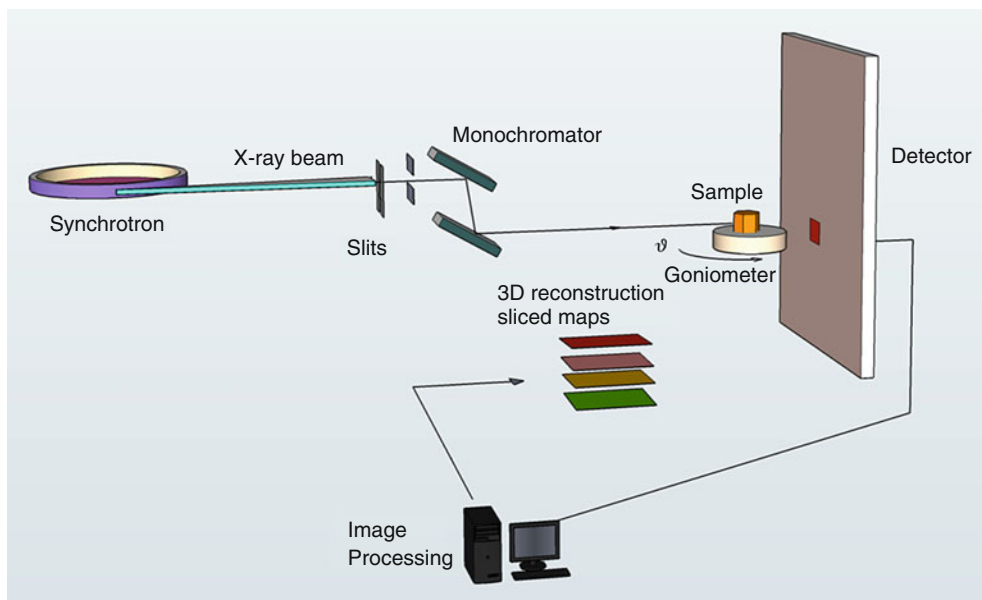
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Tomography has its roots in radiology: an X-ray beam hits a sample and the transmitted beam is recorded by a detector. The ratio of the transmitted to incident intensities will depend on the line integral of the absorption coefficient μ of the materials (which increase with the atomic

number Z) along the beam path in the sample. The resulting image will thus be a 2D projection of the volumetric absorption coefficient of the sample itself. In tomography many 2D images (radiography) are acquired at different sample orientations, for a total angle of 180° . The images are then combined together through a mathematical algorithm in order to give a 3D reconstruction, in the form of sliced 2D maps, of the different absorption coefficient inside the sample, clearly related to its chemical composition.

Synchrotron X-ray sources are unique in their properties for tomographic analysis. The intense synchrotron X-ray beam allows the resolution of subtle variations in absorptivity due to an extremely good signal-to-noise ratio. Moreover, a synchrotron X-ray beam can be considered essentially parallel which simplifies the mathematical treatment of image reconstruction, which actually assumes a parallel beam. Synchrotron radiation can be tuned for the optimization of the contrast between the chemically different constituents of the sample and for avoiding aberrations originating from the use of polychromatic beams. Finally, exploiting the partial coherence of a synchrotron X-ray beam, “phase contrast” microtomographic techniques, based on the different refractive index of different materials, can be used in order to gain further resolution in image reconstruction. On the whole, synchrotron radiation-computed microtomography (SR- μ CT) allows a spatial resolution on μm and even sub- μm order which results in a digital reconstruction of the scanned volume apt for qualitative and quantitative analysis (Bonse and Busch 1996).

The setup of a typical SR- μ CT experiment requires an X-ray source in the range of the hard X-ray region (from 8 keV upward) having a linear size of few tens of μm or less. The X-ray beam is monochromatized and reduced to the appropriate size by a slits system. The sample, generally of few mm in linear dimensions, is mounted on a holder and fitted onto a goniometer for proper orientations. Images are typically collected from a 2D detector which is often a scintillator optically coupled with a high-resolution CCD camera with a small pixel size. Depending on the beamline setup, focusing elements may also be present



X-Ray Synchrotron Microtomography, Fig. 1 Schematic representation of a synchrotron radiation microtomography experiment

before and after the sample in order to gain further resolution. Given the high brightness of the synchrotron beam, hundreds to thousands of images can be collected in a relatively small amount of time. Image processing is computed offline by using appropriate algorithms such as the “filtered back projection” or “direct Fourier inversion” methods which are found in dedicated image reconstruction software packages (Fig. 1).

SR- μ CT is a valuable tool in membrane structure analysis as provided by a nondestructive method for the investigation, at the micrometric size, of both the bulk and the interface structure of the membrane. Tomographic methods do not require specific sample preparation, finally giving a high-resolution 3D representation of the “native” sample under study.

SR- μ CT has been widely used in order to gain insights into the water distribution in polymer electrolyte membrane fuel cells (PEMFC) in response to various operation conditions. By using SR- μ CT the correlation between the wetness of the polymer electrolyte membrane, its structure, and its proton conductivity has been established (Manke et al. 2011).

A typical application of SR- μ CT to membrane science is the structural investigation of the membrane porosity. Exploiting the different absorption coefficient between the polymer and water is possible to investigate the porosity of the membrane in a quantitative way. Different porosity across the membrane is easily spotted from 3D sample reconstruction, and an estimation of the shape and dimensions of the pores is also possible due to the high resolution attainable with SR- μ CT (Remigny et al. 2007).

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Young's Model

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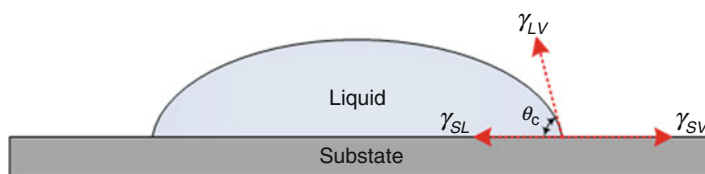
Young's model is commonly used to illustrate the wettability of solid surfaces. To better understand this behavior, surface tension or interfacial tension has to be introduced. Surface tension is a tensor that acts perpendicularly to a line on the surface and is caused by the imbalance of attractive forces at the surface where surface atoms, molecules, or ions are surrounded by a reduced number of similar species than those in the interior or have larger distances to their nearest neighbors. This causes liquid molecules at the surface to be in an

energetically unfavorable state, and therefore the surface generates a force to minimize its free surface area. When a waterdrop rests on a perfectly smooth solid surface, it forms a spherical cap whose shape is determined by the balance of the interfacial tensions (γ) between three different phases (liquid/air/solid) (Fig. 1). The contact angle (θ_c) between the water sphere and solid can be addressed as

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_C \quad (1)$$

This was first described in Thomas Young's essay in 1805. If the value of the static contact angle is $0^\circ \leq \theta_c \leq 90^\circ$, the liquid tends to spread on the surface. It is usually referred to as hydrophilic or oleophilic surface in terms of aqueous or oily liquids, respectively. If the value of the contact angle is $90^\circ < \theta_c \leq 180^\circ$, the wet area tends to shrink. It is then referred to as hydrophobic or oleophobic surface in terms of aqueous or oily

Young's Model, Fig. 1 A drop of water on solid surface. The contact angle (θ_c) is the balance of three different interfacial tensions (Hsu 2010)



liquid, respectively. Surfaces with the water contact angle between 150° and 180° are usually called superhydrophobic.

Cross-References

► [Superhydrophobicity](#)

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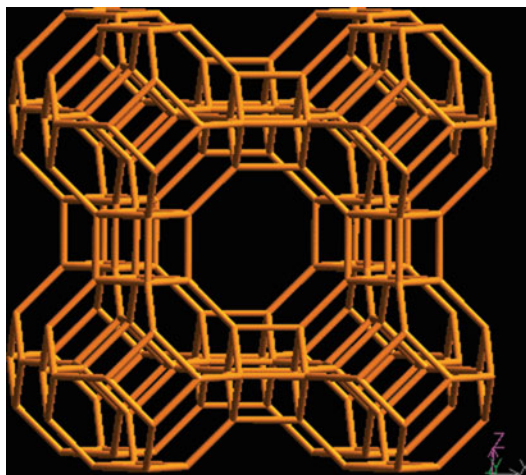
Zeolite A Type

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Zeolite A, also known as LTA (Linde Type A), belongs to the family of aluminosilicate molecular sieves. It is characterized by the formula $[(\text{Na}^+_{12}(\text{H}_2\text{O})_{27})_8[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]_8$ which corresponds to its most common hydrated sodium form (International Zeolite Association -IZA). Sodium ions in zeolite A can be exchanged with other cations such as lithium (Li-LTA), potassium (K-LTA), or calcium (Ca-LTA) (Townsend and Coker 2001). The principal building units of zeolite A are sodalite cages which are connected by four-membered rings forming a three-dimensional (3D) network (Fig. 1). These cages consist of central cavities of 11.4 Å in diameter (supercage) interconnected by eight-ring openings with a 4.1 Å aperture, thus forming a remarkably open zeolite framework with a high void volume fraction of 47 % (McCusker and Baerlocher 2001). The structure is cubic, represented by $a_0 = 11.919$ Å and the space group Pm-3m. When Na^+ is exchanged with the larger K^+ , the pore opening is reduced to approximately 3 Å

(K-LTA or 3A zeolite). In the case that Ca^{2+} replaces 2Na^+ , the pore opening increases to approximately 5 Å (Ca-LTA or 5A zeolite). Due to aperture size, the Na-LTA zeolite is also called 4A zeolite.

Zeolite A does not occur in nature and must be prepared synthetically by hydrothermal crystallization of reactive alkali metal aluminosilicate gels at low temperatures (~ 100 °C) and pressures (autogenous) under alkaline condition (pH typically higher than 12) (Yu 2007). Since its discovery at the Union Carbide Corporation Laboratories (Linde Division-Union Carbide) in the 1950s (Reed and Breck 1956), zeolite A has been largely investigated and applied at large scale for a variety of separations and purifications (Flanigen 1980). Due to its high water adsorption capacity, LTA zeolite has been first used as a desiccant for technical gases and liquids. In 1959 Union Carbide marketed the IsoSiv process for normal isoparaffin separation, representing the first major bulk separation process using true molecular sieving selectivity. The supercage structure revealed also useful for spacio-specific catalysis, such as paraffin cracking. Owing to its active ion exchange properties, zeolite A is also widely used in detergents since the mid 1970s, particularly as a replacement for the environmentally harmful phosphates for water softening. In



Zeolite A Type, Fig. 1 The type A zeolite structure – view along [100] direction (International Zeolite Association (IZA))

1999, Mitsui Engineering and Shipping Co. Ltd. manufactured the first LTA membranes to the market for the dehydration of ethanol, which was a milestone in the commercialization of zeolite A as a continuous selective barrier (Morigami et al. 2001).

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Zeolite Membrane

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Synonyms

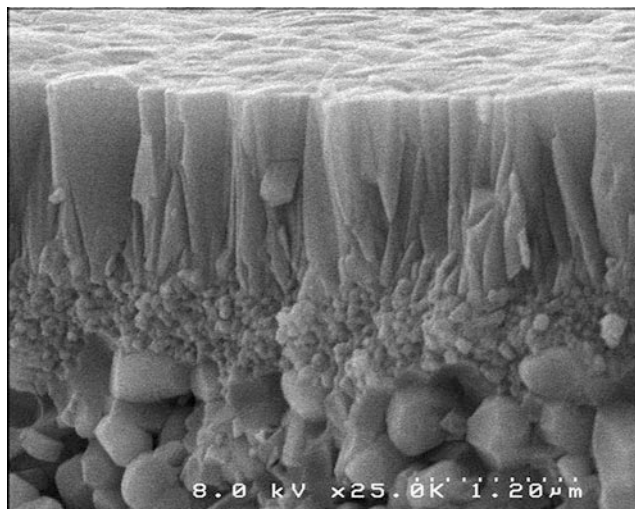
Zeolite membrane: Synthesis

Zeolite membranes are selective barriers, which can be supported or not, and prepared with well-defined aluminosilicate crystalline structures having a uniform and well-defined porous framework. Zeolites are attractive molecular sieve materials which have been used for a long time as adsorbents, catalysts, and softeners in detergents (ion-exchange properties). Since the early 1990s, zeolite membranes attracted considerable attention in many research and industrial groups, exploring their potential for the continuous separation of liquids, gas, and vapors, for chemical synthesis, pollution abatement, catalytic reactors, micro-reactors, sensors, electrodes, and optoelectronic devices (Caro and Noack 2008; Julbe 2007). Among the 229 currently known zeolitic framework type codes assigned to date by the [International Zeolite Structure Commission \(www.iza-online.org\)](http://www.iza-online.org), less than 10 % have been prepared in a form of membrane. The most studied membrane structures are LTA, MFI, CHA, SOD, DDR, FER, MEL, MFI, ERI-OFF, MOR, FAU, and BEA types (www.iza-online.org).

Several strategies have been developed for preparing zeolite membranes (supported or self-supported), such as embedding methods, in situ hydrothermal synthesis or seeding, and secondary growth (Julbe 2007). Embedding is typically used for the preparation of composite membranes (often referred as mixed matrix membranes) containing zeolite particles dispersed in a bulk matrix, generally a polymer. Zeolite membranes are usually supported, anchored, or grown on/in a porous supports with adapted mechanical, thermal, and chemical resistance (typically ceramics or metals). The seeding and secondary growth

Zeolite Membrane,

Fig. 1 MFI zeolite membrane obtained by secondary growth on a porous α - Al_2O_3 support (Motuzas et al. 2006)



strategy is now considered as the most attractive method for preparing a variety of zeolite (e.g., LTA, MFI, SOD, FAU, CHA, DDR) and zeolite-type (e.g., MCM, MOF) membranes. It confers improved flexibility for controlling crystal growth and film microstructure with high reproducibility and scalability compared to direct in situ hydrothermal synthesis (Motuzas et al. 2006). Supported MFI membrane prepared by secondary growth from a layer of silicalite-1 seeds is shown in Fig. 1. Concerning zeolite membrane industrialization, LTA membranes were the first to be prepared at large scale by Mitsui Engineering and Shipbuilding Co. for the dehydration of ethanol (Kodo et al. 1997). Other companies or research centers, including IKTS/Inocermic in Germany, ECN and Pervatech in the Netherlands, Kühni in Switzerland, and Hitachi Zosen in Japan as well as Mitsubishi Chemical Corporation, also developed zeolite-based pervaporation or vapor permeation dehydration systems (Pina et al. 2011). Recently, upscaling of SAPO-34 (Li et al. 2010) and all-silica DDR membranes (Makiko and Kenji 2012) has been considered, respectively, by Shell and NGK Insulators Ltd. for CO_2/CH_4 separation. Other types of zeolite membranes, including MFI, FAU (NaX, NaY), MOR, and T-type membranes, are considered for various applications of high industrial impact. Bussan Nanotech Research Institute Inc., namely, reported on mass production of tubular NaY

zeolite membranes for ethanol dehydration (Sato et al. 2008).

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Zeolite Membrane: Synthesis

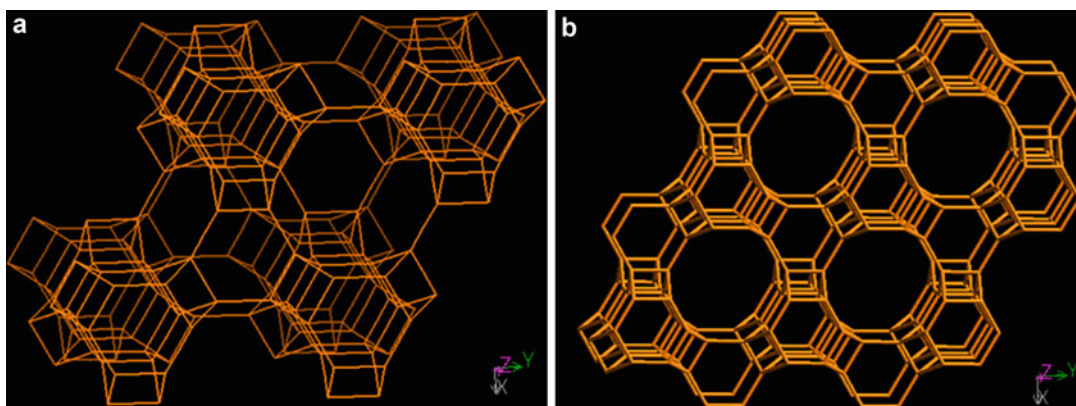
► Zeolite Membrane

Zeolite T Type

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Zeolite T (Linde type T) is a crystalline aluminosilicate with hexagonal symmetry. Its typical formula is $0.3\text{Na}_2\text{O} \cdot 0.7\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6.9\text{SiO}_2 \cdot 7.2\text{H}_2\text{O}$. It corresponds to a disordered intergrowth of erionite and offretite structures in which the more open offretite (12-ring main channels parallel to the c-axis and 8-ring sub-channels normal to the c-axis with pore sizes of 0.67×0.68 nm and 0.36×0.49 nm, respectively) (Fig. 1) is interspersed at intervals with the tighter erionite units (8-ring channels parallel to the c-axis with pore size of 0.36×0.51 nm) (Spivey et al. 1992). The framework structures of offretite and erionite are closely related, and the synthesized zeolite T is mainly composed of the offretite phase with only small amounts of erionite

sheets. Due to the specific position of single erionite unit cells at the end of the large pore of offretite, erionite controls the diffusion path by forcing the molecules to pass through the small 8-rings erionite rings. Pure erionite and offretite phases can be obtained only in the presence of an organic template, whereas intergrowth-type zeolite T can be synthesized without any template. Zeolite T, with intermediate Si/Al ratio of 3–4, is acid resistant and thermally stable while remaining hydrophilic. Its high acid resistance often overpasses other more common zeolites such as A, X, and Y. Zeolite T can be used for the selective adsorption or drying of acid gases and liquids at high temperatures. Both erionite and intergrowth offretite/erionite zeolite types have been reported as very attractive materials for catalysis or selective barriers applicable in conversion of methanol to $\text{C}_2\text{--C}_5$ olefins, selective catalytic dewaxing, and molecular sieving of n-butane (Yang and Evmiridis 1996). Zeolite T membranes have enormous potential for industrial dehydration processes, e.g., separating water from organic liquids in acidic environment, such as esterification hybrid process (Zhou et al. 2009). Due to their molecular sieving properties, zeolite T membranes have been also considered for gas separation applications, namely for separating CO_2/N_2 and CO_2/CH_4 mixtures up to 473K (Cui et al. 2004, see also Zhang et al. 2013).



Zeolite T Type, Fig. 1 (a) The erionite-type zeolite, (b) the offretite-type zeolite – view along [001] direction (International zeolite association (IZA))

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Zeolite X Type

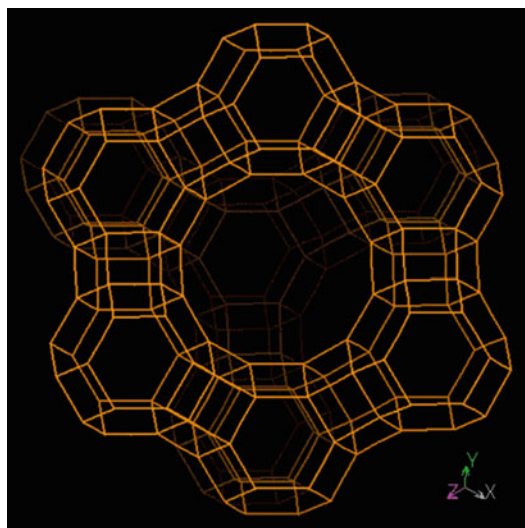
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Zeolite X, together with zeolite Y, belongs to the family of aluminosilicate molecular sieves with a faujasite-type structure (FAU). It is characterized by the formula $[(Ca, Mg, Na_2)_{29} (H_2O)_{240} [Al_{58}Si_{134}O_{384}] - FAU$ (International zeolite association (IZA)). Faujasite is a rare zeolite, although its synthetic counterparts Linde X and Linde Y are largely used as sorbents and catalysts. Zeolite X differs from zeolite Y by its Si/Al atomic ratio which is typically in the range from 1 to 1.5 for the X and higher for the Y-type zeolite. High Si/Al ratio is desirable towards thermal stability, a property that is less favorable to zeolite X. The 24 tetrahedra cuboctahedral units (sodalite cages) in the FAU framework type are arranged in the same way as the carbon atoms in diamond. They are connected via hexagonal prisms (double six rings) forming a three-dimensional porous channel

structure along [110], characterized by 12 oxygen ring window openings with the aperture of 8 Å and supercages of approximately 12 Å (McCusker and Baerlocher 2001). The FAU-type zeolite supercage viewed along [111] is shown in Fig. 1 (International zeolite association (IZA)).

The combination of large void volumes and large pore openings in a three-dimensional channel system makes FAU molecular sieve ideal for many catalytic applications. This zeolite is also attractive for its ion exchange and adsorptive properties.

The combination of Si⁴⁺ and Al³⁺ results in a deficiency of positive charge which is balanced by exchangeable cations. Due to its very low Si/Al ratio, the zeolite X framework provides a large number of cation exchange sites balancing the framework aluminum, thus leading to high cation contents and exchange capacities. Zeolite X is generally synthesized by hydrothermal crystallization of reactive alkali metal aluminosilicate gels or clear solutions at low temperature (70–300 °C, usually 100 °C) and pressure (autogenous) under alkaline conditions. Starting typically from sodium aluminate and sodium silicate, zeolite



Zeolite X Type, Fig. 1 The FAU type zeolite supercage – view along [111] direction (www.iza-online.org)

X is obtained in its Na^+ form. Zeolite NaX is a metastable phase, meaning that other types of zeolites such as P, A, or sodalite may form if the recipe is not followed carefully (Balkus and Ly 1991). For specific catalytic applications, the incorporation of various metal cations into the structure can be carried out by impregnation or ion exchange. This results in the modification of the number and nature of acid sites influencing the diffusion of reactants and products. A large variety of cationic species has been introduced into FAU frameworks. X-type zeolite has a wide range of industrial applications for gas or vapor adsorption, separation, and as catalyst. Examples of applications in chemical reactions include isomerization of 1-butene, alkylation of toluene with ethylene or methanol, and cycloaddition of carbon dioxide to ethylene oxide (Ribeiro et al. 1984). X-type zeolites can be used to adsorb an unwanted compound during decomposition reactions such as removal of alkyl hydroperoxides from ethers and olefins during hydrobromination of alkenes (Wortel and van Bekkum 1980). Alcohol dehydration by pervaporation is a potential application for X-type membranes (Zhou et al. 2012). However, in many large-scale industrial applications, its chemical analogue with Si/Al ratio higher than 1.5 (zeolite Y) has superseded zeolite X because of its higher chemical and thermal stability.

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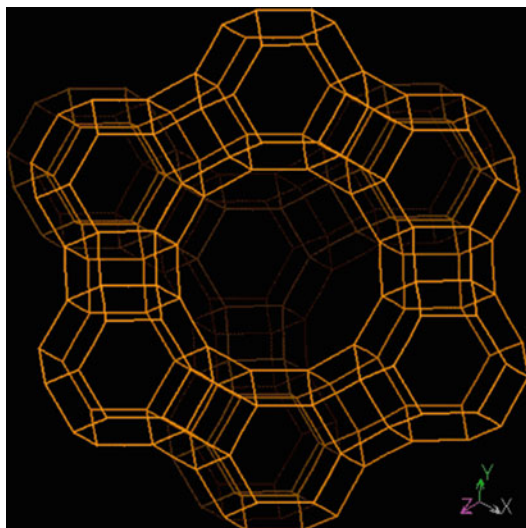
Zeolite Y Type

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Zeolite Y, together with zeolite X, belongs to the family of aluminosilicate molecular sieves with a faujasite-type structure (FAU), which is characterized by the basic formula $[(\text{Ca}, \text{Mg}, \text{Na}_2)_{29}(\text{H}_2\text{O})_{240}][\text{Al}_{58}\text{Si}_{134}\text{O}_{384}]$ –FAU (Baerlocher 2007). Faujasite is a rare zeolite, although its synthetic counterparts Linde X and Linde Y are largely used as sorbents and catalysts. Zeolite Y has a higher Si/Al atomic ratio than zeolite X (typically in the range 1–1.5). Therefore, the higher content of silica confers zeolite Y with higher thermal stability. The 24-tetrahedracuboctahedral units (sodalite cages) in the FAU framework type are arranged in the same way as the carbon atoms in diamond. They are connected via hexagonal prisms (double 6-rings) forming a 3-dimensional porous channel structure along [110], characterized by 12-oxygen ring window openings with the aperture of 8 Å and supercages of approximately 12 Å (McCusker and Baerlocher 2001). The FAU-type zeolite supercage viewed along [111] is shown in Fig. 1

The combination of large void volume and large pore openings in a 3-dimensional channel system makes this thermally stable FAU molecular sieve ideal for many catalytic applications. This zeolite is also considered for its ion-exchange and adsorptive properties. Zeolite Y is generally synthesized by hydrothermal crystallisation of reactive alkali metal aluminosilicate gels or clear solutions at low temperature (70–300 °C, usually 100 °C) and pressure (autogenous) under alkaline conditions. Starting typically from sodium aluminate and sodium silicate, the Y zeolite is obtained in its Na^+ form (Blatter and Schumacher 1991) and a replacement of the Na^+ cations by protons (leading to the H-zeolite form) is required for applications in acid catalysis. Due to the poor stability of the FAU structure in acidic media, this conversion is



Zeolite Y Type, Fig. 1 The FAU type zeolite supercage – view along [111] direction (www.iza-online.org)

done indirectly via an ammonium exchange resulting in $\text{NH}_4^+ \text{Y}$, where the cation is decomposed into ammonia and protons, thus yielding a highly crystalline H-FAU structure. Dealumination of the Y zeolite framework results in the formation of ultra-stable Y zeolite (USY) with high (hydro)thermal stability. USY prepared by thermal, hydrothermal, or chemical dealumination of zeolite Y is one of the most widely employed zeolite material in the petrochemical industry. Zeolite Y is essentially used as a Fluid Cracking Catalyst (FCC) of heavy petroleum distillates, for increasing the yield of gasoline and Diesel fuel from crude oil (Kung et al. 2000). It is also used to increase the aromatic content of refinery products in hydrocracking units, when it is associated with platinum or palladium species, deposited by either impregnation or ion exchange (Ribeiro 1984). A large variety of other applications have been reported for the Y zeolite, including the dealcoholization of beer, the removal of toxic preservatives in the pharmaceutical preparation of insulin, the slow-release of drugs, or the encapsulation of specific ions for electrocatalytic applications (Pavelic and Hadzija 2003), also in addition to simple gas phase or liquid phase separations and treatments, including membranes (Morooka et al. 1998). Bussan

Nanotech Research Institute Inc., namely, reported on mass-production of tubular NaY zeolite membranes for ethanol dehydration (Sato et al. 2008).

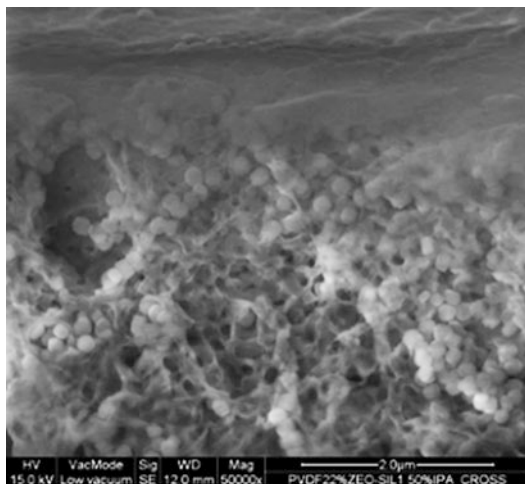
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Zeolite-Embedded Membrane

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Zeolite-embedded membranes belong to the family of composite selective barriers (also referred as mixed matrix membranes (MMMs)), which are



Zeolite-Embedded Membrane, Fig. 1 MMM with MFI zeolite particles (22 wt%) embedded in a PVDF polymer matrix (Drobek et al. 2015)

typically obtained by dispersing zeolite crystals in a bulk matrix, usually a polymer film (Bastani et al. 2013). Zeolite-filled MMMs have been intensively studied from the early 1970s as a strategy to overcome the permeability/selectivity trade-off of conventional polymeric membranes. The basic idea was to obtain a synergic effect by combining the high selectivity and permeability of zeolites with the attractive mechanical properties and economical processability of polymers. These membranes were intensively considered for difficult gas separations or pervaporation but also as interface contactors and in fuel cell applications (Jeong et al. 2010; Zornoza et al. 2011; Tricoli and Nannetti 2003). The key point of membrane efficiency bears on the selection of a relevant zeolite/polymer coupling, thus providing a good quality interfacial contact between the inorganic filler and the matrix (nonselective diffusion pathways). Several zeolite surface modification strategies, such as silanation, annealing, or Grignard treatments, have been considered to improve and optimize interfaces. Nanosize zeolite particles embedded in MMMs generally outperform MMMs prepared with micron size particles, when optimized loading and dispersion are used. Preparation of zeolite-embedded membranes (Fig. 1) is adapted from classical methods used for polymeric membranes, although membrane

processing steps and solvents that can “clog” the zeolites should be avoided. Early attempts at designing MMMs focused on gas separation using rubbery polymers such as polydimethylsiloxane (PDMS). Nowadays, glassy polymers such as polyimide (PI), polyethersulfone (PES), or copolymers are preferably used together with semicrystalline polyvinylidene fluoride (PVDF). The latter possesses excellent mechanical properties, thermal stability, and high chain movements, enabling preparation of membranes with high inorganic filler content. Typical zeolite fillers in MMMs are silicalite-1, ZSM-5, L, 3A, 4A, 5A, 13X, KY, H-SSZ-13 β -type, or SAPO-34 (Julbe 2007). Zeolite-type materials (e.g., MCM-41, MCM-48, SBA-15, ZIF) have been also considered, and highly attractive results were also obtained with the MOF (metal-organic frameworks) fillers which provide better interfacial contact with polymers (Bastani et al. 2013).

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Zeolitic Imidazolate Framework-8

► ZIF-8 Membrane

Zeta Potential

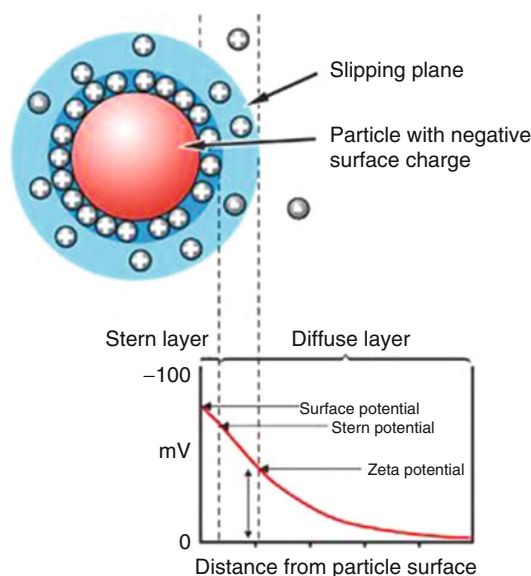
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Zeta potential: When two phases are placed in contact, there develops in general a difference in potential between them (Hunter 1981). The term zeta potential is an abbreviation for the electrokinetic potential in colloidal systems. In the colloidal chemistry literature, it is usually represented using the Greek letter zeta (ζ). The zeta potential is commonly associated with particulate systems but can also be measured for surfaces such as membranes. The zeta potential does not occur exactly at the interface, but is in fact the electric potential in the interfacial double layer at the location of the slipping plane (or outer Helmholtz plane) (Hunter 1981) versus a point in the bulk fluid away from the interface (see Fig. 1).

The zeta potential is used in DLVO theory (Hunter 1989) to describe the magnitude of the electrostatic forces (usually repulsive for liked

charged particles/surfaces) and give the potential stability of a colloidal system. For colloidal systems, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation/flocculation. When the zeta potential is low, attraction exceeds repulsion and the dispersion will flocculate. A value of 25 mV (positive or negative) is usually taken as the arbitrary value that separates low charged surfaces from highly charged surfaces. Colloids with a high magnitude of the zeta potential (positive or negative) are said to be electrically stabilized.

The zeta potential, however, is not measurable directly but can be calculated using theoretical models and experimentally determined values such as the electrophoretic mobility or the streaming potential. Electroacoustic phenomena may also be used for the calculation of zeta potential. The most known and widely used theory for calculating zeta potential from experimental data is that developed by Smoluchowski (1903). This theory was originally developed for electrophoresis; however, an extension to electroacoustics is now also available (Dukhin and Goetz 2002). Smoluchowski's theory is powerful because it is valid for dispersed particles of any shape and any concentration. Smoluchowski's theory does have limitations in that it is only valid for thin double layers and surface conductivity is neglected. More modern, rigorous electrokinetic theories that are valid for any zeta potential have been developed and are available in the literature (Dukhin and Semnikhin 1970; O'Brien and White 1978).



Zeta Potential, Fig. 1 Illustration of slipping plane for a spherical particle (MRK654-01)

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Zeta Potential Measurement

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Zeta potential measurement of a solution is calculated indirectly by determining the electrophoretic mobility of particle immersed in a liquid under an electrical field. The electrophoretic velocity can be determined in different ways (Merkus 2014):

- Directly under microscope.
- Measuring the Doppler shift of the frequency of scattered light (based on laser Doppler electrophoresis (LDE)) or the phase shift (based on phase analysis light scattering (PALS)), by light scattering systems.
- Measuring the colloid vibration potential (CVP) or current (CVC) or the electrokinetic sonic amplitude (ESA), by electroacoustic instruments.

Once the particle velocity was determined, knowing the electrical field applied and taking into account the viscosity and the dielectric constant of the sample, it is possible to determine the zeta potential applying Henry Eq. 1:

$$U_e = \frac{2\varepsilon z f(Ka)}{3\eta} \quad (1)$$

where z is the zeta potential, U_e is the electrophoretic mobility, ε is the dielectric constant, η is viscosity, and $f(Ka)$ is the Henry function. Henry function is related to the ratio of the particle radius and the thickness of the double layer. For $f(Ka)$ determination, two values are generally used (1.5 and 1.0).

The value of 1.5 is generally used for systems that fit the Smoluchowski model (particles larger than 0.2 μm with) and when the analysis was carried out in aqueous media and moderate electrolyte concentration (electrolyte concentration more than 10^{-3} molar). The value of 1 is generally used for small particles in low dielectric constant and also for sample in nonaqueous media.

Particles with zeta potential between -10 and $+10$ mV are considered neutral; greater than $+30$ mV are strongly cationic while less than -30 mV strongly anionic.

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ZIF

► ZIF-8 Membrane

ZIF-8 Membrane

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Synonyms

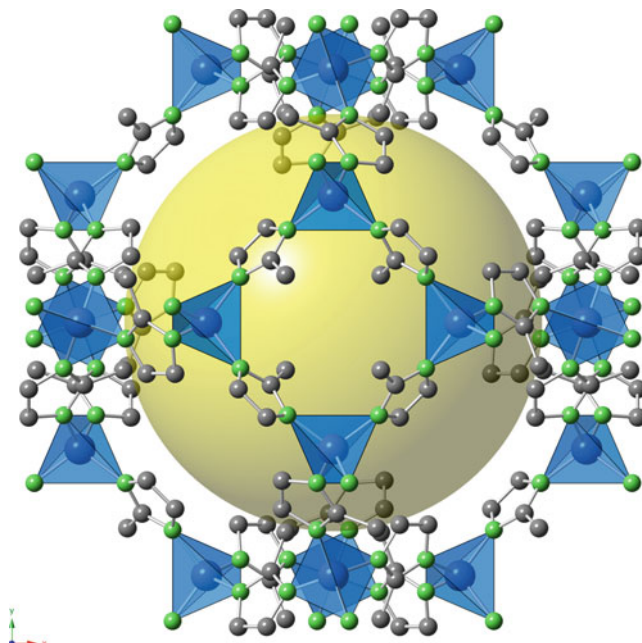
Metal-organic framework; MOF; Zeolitic imidazolate framework-8; ZIF

ZIF-8 Membrane Properties

Zeolitic imidazolate framework-8 (ZIF-8) membrane is a separation membrane which is

ZIF-8 Membrane,

Fig. 1 Structure of the zeolitic imidazolate framework-8 (H atoms are omitted for clarity)



fabricated using ZIF-8. ZIF-8 is classified as part of metal-organic frameworks (MOFs), which is connected with the coordination bonds between metal ions and organic ligands. ZIF-8 is composed of zinc atoms and 2-methylimidazole as a ligand that forms a sodalite topology having large cavities with a diameter of 1.16 nm, which are connected through a small pore aperture of 0.34 nm diameter (Fig. 1, Park et al. 2006).

The adsorption and diffusion characteristics of ZIF-8 have been investigated. It is reported that the ratio of the diffusion rate coefficients for propylene and propane is about 100–125, whereas the equilibrium adsorption capacities are almost identical (Li et al. 2009; Zhang et al. 2012b). Thus, it is concluded that the effective aperture size of ZIF-8 pore opening is between 0.40 and 0.42 nm, which are the van der Waals diameters of propylene and propane, respectively. The effective aperture size of ZIF-8 pore opening is larger than that obtained from crystallographic data (0.34 nm) due to the flexibility of the ZIF-8 pore structure. Therefore, ZIF-8 is recognized as a material for the separation of propylene/propane by molecular sieving.

Several methods have been reported for the preparation of the ZIF-8-based membranes. One

of the preparation methods for the ZIF-8 membrane is the mixed matrix membranes (MMMs), which combine the ZIF-8 particles with the polymer matrix. Preparation and the permeation properties are reported for several applications such as CO₂/N₂ separation (Lively et al. 2012), water/alcohol separation (Shi et al. 2012), and propylene/propane separation (Askari and Chung 2013; Zhang et al. 2012a).

ZIF-8 membranes with pure ZIF-8 selective layers are prepared from direct growth method, secondary growth method, and counter-diffusion method. In the direct growth method, ZIF-8 membranes are directly formed under the solvothermal conditions (Bux et al. 2009; McCarthy et al. 2010; Shah et al. 2013; Xu et al. 2011). Secondary growth method starts with the preparation of the seed layer followed by the growth of the ZIF-8 layer under solvothermal conditions (Bux et al. 2011; Ge et al. 2012; Kwon and Jeong 2013a; Li et al. 2013; Liu et al. 2014; Pan et al. 2012; Tao et al. 2013; Venna and Carreon 2010). Pan et al. reported the effective separation of propylene/propane with ZIF-8 membranes with selectivity up to 50 for an equimolar mixture of propylene/propane (Pan et al. 2012). Successively, Liu et al. also reported ZIF-8 membranes

with excellent propylene/propane separation performance (Liu et al. 2014). From the other method, counter-diffusion method, ZIF-8 layer is formed from the interface of the zinc salt and the 2-methylimidazole solutions, which is advantageous for decreasing the defect in the ZIF-8 layer. Kwon et al. reported the preparation and the permeation properties of ZIF-8 membranes with the selectivity up to 55 for an equimolar mixture of propylene/propane (Kwon and Jeong 2013a, b). Hara et al. reported the preparation of ZIF-8 membranes with the ideal separation factor up to 59, and the contribution of the diffusive separation of propylene/propane was determined from the single-component gas permeation properties (Hara et al. 2014).

ZIF-8 membrane has a high potentiality for various applications especially for the propylene/propane separation owing to its characteristic pore structure. Various researches are in progress for the preparation of the ZIF-8 membranes with both high permeance and high selectivity and also for the characterization of the membrane permeation properties.

Cross-References

► Metal-Organic Frameworks (MOFs)

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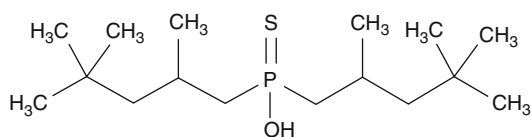
Zinc Recovery by Supported Liquid Membrane

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Zinc is an essential element for life, being indispensable for humans, animals, and plants. It is also extensively used by humankind in many industrial applications (electrical or automotive industries, surface treatments, etc.), both directly and as oxides, sulfides, or in alloys such as brass.

Recovery of zinc by supported liquid membranes has been done at a laboratory scale. It may be carried out by using organic extractants commercially available, mostly phosphoric acid derivatives such as bis(2,4,4-trimethylpentyl) monothiophosphinic acid Fig. 1, bis(2-ethylhexyl) hydrogen phosphate, or bis(2,4,4-trimethylpentyl) phosphinic acid.



Zinc Recovery by Supported Liquid Membrane, Fig. 1 Chemical structure of bis(2,4,4-trimethylpentyl) monothiophosphinic acid

Cross-References

- [Cobalt Removal and Recovery by Supported Liquid Membranes](#)

Zirconium-Phosphate (ZrP)-Filled Nafion Membrane

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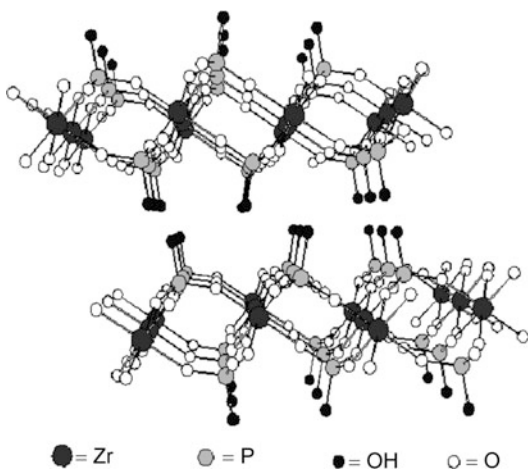
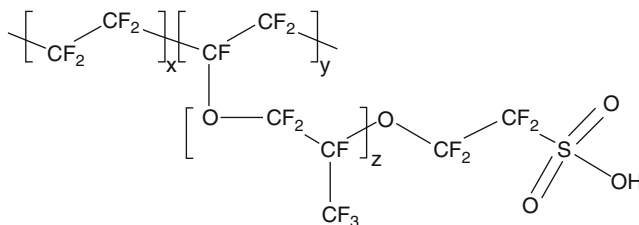
Zirconium phosphate (ZrP)-filled Nafion membranes are a class of organo-inorgano composite membranes consisting of nanoparticles of an inorganic filler (ZrP) dispersed within a polymer matrix based on a perfluorosulfonic acid ionomer (Nafion).

Nafion is a sulfonated tetrafluoroethylene-based polymer, with perfluorovinyl ether side chains, terminated with sulfonic superacid groups (Fig. 1) (Mauritz and Moore 2004). According to the many different structural models, the morphology of Nafion membranes consists of hydrophilic channels, made up by the clustering of the sulfonic acid functional groups which are responsible for the proton transport; these channels are delimited by the hydrophobic perfluorinated polymer backbone, which assures thermal, chemical, and mechanical stability, especially at temperatures <80 °C.

Zirconium phosphate represents the earliest example of metal(IV) phosphate and phosphonate-layered compounds. The structure of the α -type ZrP is built up by the packing of layers made of planes of zirconium atoms bonded, on both plane sides, to monohydrogen phosphate groups (Fig. 2) (Clearfield and Costantino 1996). ZrP has been extensively studied as filler of polymers, especially ionomers (Alberti and Casciola 2003; Neburchilov et al. 2007) due to its thermal and chemical stability, to its proton conduction

Zirconium-Phosphate (ZrP)-Filled Nafion Membrane,

Fig. 1 Chemical structure of Nafion



Zirconium-Phosphate (ZrP)-Filled Nafion Membrane, Fig. 2 Schematic representation of ZrP-layered structure

properties, and to its ability to intercalate, within the layers, organic molecules and macromolecules, such as polymer chains, which could promote the layer separation (exfoliation) and their dispersion within the polymer matrix.

Three main synthetic procedures are known to prepare Nafion-ZrP membranes (Alberti et al. 2007):

- i. Dispersion of preformed filler particles in the polymer dispersion. According to this procedure, colloidal dispersions or gels of highly exfoliated ZrP particles are mixed with a Nafion dispersion in the same solvent. The membrane is then obtained by solution casting, followed by solvent evaporation.
- ii. In situ ZrP precipitation: this method is based on the use of preformed Nafion membranes and on the exchange of the membrane protons with zirconium cationic species, followed by treatment with phosphoric acid solutions.

- iii. "Precursor solution" method: a ZrP precursor solution in polar aprotic solvents is added to a Nafion dispersion in the same solvent: the precipitation of the ZrP particles occurs during the solvent evaporation from the cast mixture.

The properties of the composite membranes depend on the filler morphology and loading. It was found that the presence of the ZrP particles in Nafion membranes:

- Decreases the degree of crystallinity of the polymer (Bauer and Porada 2004; Alberti et al. 2007; Casciola et al. 2008)
- Increases the mechanical strength of the membranes (Alberti et al. 2007; Casciola et al. 2008)
- Decreases the proton conductivity with respect to the neat polymer (Alberti et al. 2007; Casciola et al. 2008)
- Improves the fuel cell performances at temperatures $>80^{\circ}\text{C}$ (Yang et al. 2004)
- Decreases the methanol permeability with respect to the neat polymer (Bauer and Porada 2004), especially when ZrP particles with high aspect ratio are employed as filler (Casciola et al. 2009)

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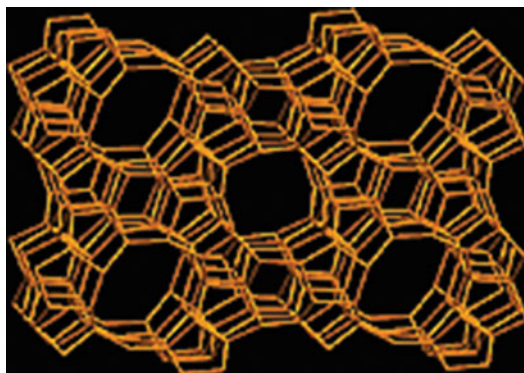
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ZSM-5 Zeolite Membrane

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ZSM-5 (Zeolite Socony Mobil-5, patented by Mobil oil company in 1975) is a high silica zeolite with a MFI framework structure (Mobil Five) characterized by the formula $[(\text{Na}_x(\text{H}_2\text{O}))_{16}[\text{Al}_x\text{Si}_{96-x}\text{O}_{192}]]$, where $x < 27$ (International Zeolite Association-IZA). It is composed of pentasil units which are linked to form pentasil chains connected via oxygen bridges to form corrugated sheets with 10-ring holes (Fig. 1). Oxygen bridges between these sheets result in a 3-dimensional system with straight 10-ring channels parallel to the corrugations (along y) and sinusoidal 10-ring channels perpendicular to the



ZSM-5 Zeolite Membrane, Fig. 1 The MFI type structure – view along [010] direction (International Zeolite Association-IZA)

sheets (along x). The MFI 3D framework, consisting of straight and zigzag channels, is a rather complex zeolite framework type. The structure is orthorhombic (space group Pnma) at high temperatures, but a phase transition to the monoclinic space group occurs on cooling below the transition temperature, i.e., between 300 and 350 K. Because the pore openings are 10-rings (straight channels have circular openings of 0.54–0.56 nm and sinusoidal channels have elliptical openings of 0.51–0.55 nm), the shape selectivity for sorption and catalysis resulted in many applications of this zeolite in refinery and petrochemical industry, including for hydrocarbon isomerization and alkylation of hydrocarbons (McCusker and Baerlocher 2001). ZSM-5 does not occur in natural rocks and must be prepared synthetically in basic media at high pressures (autogenous) and temperatures (typically 120–200 °C) from alumina and silica sources and eventually in the presence of structure directing agents such as tetrapropylammonium-based compounds. Seeds with the MFI structure can also be used to fasten the synthesis kinetics and generate uniform supported layers/membranes. The type of the raw materials and the presence/absence of template are of the utmost importance on the crystal morphology and the distribution of aluminum atoms in the framework, leading to the formation of zeolite catalyst with acidic properties which could be effectively

controlled during the synthesis. The acidity is proportional to the Al content and a number of positive charges (e.g., Na^+ or H^+) attached to the framework which tends to keep the zeolite charge neutral. Due to its high acidity, ZSM-5 is an active heterogeneous catalyst for acid-catalyzed reactions. ZSM-5 membranes have been largely investigated in the literature, for gas separation (e.g., CO_2 (Bernal et al. 2004)), pervaporation (organic dehydration or removal of organics from water), and applications in catalytic reactors (Julbe 2007). Xylene isomerization favoring paraxylene production is a typical example where molecular sieving through ZSM-5 leads to a faster diffusion of the latter. A series of additives has been introduced within the ZSM-5 membranes, either by postsynthetic modification or directly during the synthesis, to modify either the surface properties or the channel size of the zeolite membrane. Catalytic cracking of methyldiethoxysilane is an example of postmodification, yielding attractive H_2 separation properties for the modified ZSM-5 membranes, up to 500 °C (Wang and Lin 2012; Hong et al. 2005).

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 - Central Nervous System in Relation to Membranes
 - Ceramic Membrane for Pervaporation
 - Ceramic Membranes
 - Ceramic Multilayer Membranes
 - Ceramic Supported Polymer Composite Membranes in Pervaporation
 - CH₄/N₂ Separation
 - CHA Zeolite Membrane
 - Characterization of Porous and Dense Membranes
 - Charged Mosaic Membrane
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 - Chemical and Electrochemical Equilibrium in Membrane Systems
 - Chemical Binding of Biomolecules to Membranes
 - Chemical Cleaning of Membranes
 - Chemical Industry and Membrane Operations
 - Chemical Looping
 - Chemical Membrane Reactors
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 - Chemometrics
 - Chiral Drug Separation by Membranes
 - Chlorination Process
 - Chlorine-Resistant Polymeric Membranes
 - Chloromethylation and Amination of Polymers (for AEM)
 - Chromium Transport Through Ion Exchange Membranes
 - Citric Acid Recovery by Electrodialysis
 - Cleaning Cycle of Fouled Membranes
 - Cleaning Effectiveness
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 - Cleaning-in-Place (CIP) Systems
 - Closed-Loop Cascade Diafiltration
 - Co (II) Ions Separation by Supported Liquid Membranes
 - CO Inhibition to Pd-Based Membrane
 - CO Selective Oxidation
 - Coacervation
 - Coagulation Bath
 - Coagulation Medium

- Coagulation Medium (also Known as Nonsolvent Bath, Coagulation Bath, Phase-Inversion Medium, Precipitating Medium)
- Cobalt Removal and Recovery by Supported Liquid Membranes
- Cobalt Removal and Recovery with Strip Dispersion
- Cold Plasma
- Combined Fouling Index (CFI)
- Complexation–Ultrafiltration Process for Heavy Metal Removal from Effluents
- Composite Membrane with Inorganic Fillers: Electrolyser Application
- Composite Membrane with Inorganic Fillers: Fuel Cell Application
- Computational Fluid Dynamics (CFD) and Membranes
- Computer-Aided Methods and Tools
- Computer-Aided Models
- Concentration Polarization Coefficient (CPC)
- Concentration Polarization in Gas Separation
- Concentration Profile
- Constant-Volume Diafiltration
- Contacto-Type Catalytic Membrane Reactor
- Continuous Diafiltration: Cocurrent and Countercurrent Modes
- Continuous Electrodeionization
- Continuous Membrane Fermentor (CMF)
- Continuous Stirred Tank Membrane Reactor (CST-MR)
- Controlled Delivery
- Controlled Drug Release
- Controlled Release
- Controlled Release by Membrane
- Controlled Release Dose
- Controlled Release Kinetics
- Convective Transport
- Conventional Ball Milling and Calcination
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- Copolyimide Precursors
- Copper Removal and Recovery by Supported Liquid Membranes
- Core Shell Particles
- Corrosion
- Co-sintering Method for Ceramic Membrane Preparation
- Cost-Effective Gas Separations
- Critical Flux
- Cross-Flow Filtration
- Cross-Flow Membrane Bioreactor
- Cross-Flow Membrane Module
- Cross-Link
- Cross-Linkable Copolymer Membranes
- Cross-Linked Aromatic Polyamide Membranes
- Cross-Linked Layer-by-Layer Membranes
- Cross-Linked Poly(ethylene oxide) Membranes
- Cross-Linked Polyamide Membranes
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- Dead-End Filtration
- Dealcoholization by Pervaporation
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- Decatungstate, Catalytic Membrane Containing
- Decentralized Wastewater Treatment System
- Dechlorination Process
- Definition of Various Membrane Processes
- Degenotoxification
- Degree of Mixedness
- Dehumidification of Atmospheric Air by Membrane Technology
- Dehydration
- Dehydration of Solvents with Membranes
- Dehydrogenation Reactions
- Dehydroisomerization of N-Butane to Isobutene
- Deionization by Membrane Operations
- Dense Membranes
- Density Functional Theory Modeling of Membrane Systems
- Design of Experiment (DOE)
- Detergents
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 Direct Contact Membrane Distillation (DCMD)
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E

Ease of Expansion in Gas Separation
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- Electrooxidation
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H

H₂ Permeation Through Pd-Based Membranes
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Hydrocarbon Branching
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I

Ideal Gas Selectivity
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 - Membrane Stripping
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 - Membrane Wettability
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 - Membrane-Cryogenic Hybrid Processes
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 - Membranes for CO₂ Capture from Flue Gas
 - Membranes for Natural Gas Sweetening
 - Membranes for Seawater Desalination
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 - Membranes in Antibiotic Production
 - Membranes in Nuclear Waste Treatment
 - Membranes in the Chlor-Alkali Industry
 - Membrane Permselectivity
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 - Membranes Used for Membrane Emulsification
 - Mesophilic Organisms
 - Mesosopic Transport Simulation
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 - Microalgae Concentration
 - Microcapsule Membranes
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Olive Mill Wastewater Treatment by Membrane
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 Polyethersulfone Membrane

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Polyethylene Oxide
Polymer Electrolyte Membrane Fuel Cell (PEMFC)
Polymer Inclusion Membranes
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Polymeric Catalytic Membranes
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Spiral Wound Module

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